

Strategic Environmental Research and Development Program

Distribution and Fate of Energetics on DoD Test and Training Ranges: Interim Report 5

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Interim report

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ABSTRACT: The potential for generation of environmental contamination in the form of residual munitions constituents during live-fire training activities on military ranges is a significant concern. The objectives of this project were to determine the nature and distribution of the potential contamination and to define transport properties of the constituents. Surface soils associated with impact craters, targets areas, and firing points on U.S. and Canadian ranges were investigated. Residues from high-order, low-order, unconfined charge, and blow-in-place detonations were characterized. Analyses of these residues defined concentrations and spatial distributions of munitions constituents under various firing activities for specific munitions. Special emphasis was placed on developing representative sampling strategies. Residues from low-order detonations were assayed to develop a source term for use in fate and transport models and risk assessment models. Pertinent data from the Massachusetts Military Reservation was reviewed and compared to the database for other ranges. Results demonstrate that a systematic composite sampling protocol developed for artillery ranges improved reproducibility over random composite or discrete sampling protocols. Results of low-order detonation studies confirmed an inverse relationship between energy of detonation and residue generated. While directionality was unpredictable, the residue was dominated by larger particles, which resulted in conservation of the pre-detonation composition of the munition. Several heavy metals were of significant concern at antitank target areas, hand- and rifle-grenade ranges, and small arms ranges. Explosives detected were specific to range activity. Results of sympathetic detonation tests demonstrated that cracking was initiated by flying shrapnel rather than by the shock wave of the first detonation. High-order detonations generate by blow-in-place detonations resulted in low-milligram quantities of explosives residue. The results of this project define the relationship between various training activities and residues of energetic materials, which provides a basis for sound management strategies supporting training range sustainment without conflicting with objectives of environmental stewardship.

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Abbreviations

AcN Acetonitrile

ADNTs Aminodinitrotoluenes

2ADNT 2-amino-4,6-dinitrotoluene

4ADNT 4-amino-2,6-dinitrotoluene

AEC Army Environmental Center

2A4NT 2-amino-4-nitrotoluene

4A2NT 4-amino-2-nitrotoluene

BG Background sample

BIP Blow-in-place

CCME Canadian Council of Ministers of Environment

CF Canadian Forces

CFB Canadian Forces Base

CFTO Canadian Forces Technical Order

COC Contaminants of concern

CG Camp Guernsey, Wyoming

CHPPM Center for Health Promotion and Preventive Medicine

CRREL Cold Regions Research and Engineering Laboratory

DARPA Defense Advanced Research Projects Agency

DCC Defence Construction Canada

DGE Director General Environment, Canadian Department of

National Defence

DLE Director Land Environment, Canadian Department of

National Defence

3,5DNA 3,5-dinitroaniline

1,3DNB 1,3-dinitrobenzene

DND Department of National Defense

2,4DNT 2,4-dinitrotoluene

2,6DNT 2,6-dinitrotoluene

DNT Dinitrotoluene

DoD U.S. Department of Defense

DoE U.S. Department of Energy

DRDC Defense Research and Development Canada

DRDC-Valcartier Defense Research and Development Canada - Valcartier

EBW Exploding bridgewire

ERF Eagle River Flats

ASQG Agricultural Soils Quality Guidelines

EL Environmental Laboratory

EOD Explosive ordnance disposal

EPA U.S. Environmental Protection Agency

ERDC U.S. Army Engineer Research and Development Center

FB Fort Bliss, New Mexico

FP Firing position

FR Fort Richardson, Alaska

GC-ECD Gas chromatography—electron capture detection

GPS Global positioning system

HE High explosive

HSV High-speed video

HMX Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine, or High

melting explosive

ICP-MS Inductively coupled plasma—mass spectrometry

IR Infrared

ISQC Industrial soil quality guidelines

LAW Light antitank weapon

LIS Large-increment (50–100+) samples

MBG Mean background level

MCD Main charge disruptor

MEC Munition explosive constituents

MIS Multi-increment (approximately 40) samples

MMR Massachusetts Military Reservation

3NA 3-nitroaniline

NATO North Atlantic Treaty Organization

NB Nitrobenzene

NEW Net explosive weight

NG Nitroglycerin

NT Nitrotoluene

OB/OD Open burning/open detonation

OD Open demolition

OTP Outside the demarcated plume

PEL Probable effect level

PETN Pentaerythritol tetranitrate

QA/QC Quality assurance/quality control

RDX Hexahydro-1,3,5-trinitro-1,3,5-triazine, or Research

development explosive

RPC (not an abbreviation) Laboratory, Fredricton, NB

RP-HPLC-UV Reversed-phase high performance liquid chromatography

with ultraviolet detection

RPD Relative percent difference

RSO Range safety officer

RSQG CCME residential soil quality guideline

SAR Small arms range

SARM Standard analytical reference materials

SERDP Strategic Environmental Research and Development

Program

SPE Solid-phase extraction

SQG Soil quality guidelines

SRIA Static range impact areas

TCLP Toxicity characteristic leaching procedure

TNB 1,3,5-trinitrobenzene

TNT 2,4,6-trinitrotoluene

TRI Toxic release inventory

TRL Total light radiation

USARAK U.S. Army, Alaska

USCHPPM U.S. Army Center for Health Protection and Preventative

Medicine

UXO Unexploded ordnance

WAT Wellington Antitank Range

XRT Experimental rubbery TNT

YTC Yakima Training Center, Washington

Preface

This report was prepared by the U. S. Army Engineer Research and Development Center (ERDC), Environmental Laboratory (EL), Vicksburg, MS, and the Cold Regions Research and Engineering Laboratory (CRREL), Hanover, NH, in partnership with the Defence Research and Development Canada - Valcartier (DRDC-Valcartier), Quebec, Canada, and AMEC Earth and Environmental, Inc. (AMEC), Westford, MA. The research was sponsored by the Strategic Environmental Research and Development Program (SERDP), Arlington, VA, Mr. Bradley P. Smith, Executive Director, and Dr. Jeff Marqusee, Technical Director, under Compliance Project Number CP1155. The principal investigator was Dr. Judith C. Pennington, Research Biologist, Environmental Processes and Engineering Division (EPED), EL, ERDC. Co-principal investigators were Dr. Thomas F. Jenkins, Research Chemist, Environmental Sciences Branch (ESB), CRREL; Dr. Guy Ampleman and Dr. Sonia Thiboutot, DRDC-Valcartier; and Mr. Jay Clausen, AMEC Earth and Environment, Inc.

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1 Introduction

Background

The readiness of the Armed Forces of the United States and Canada is predicated on well-trained troops and continuous enhancements of our munitions arsenal. Sustained use of live-fire training ranges is especially critical to U.S. missions abroad, which currently demand rapid and effective mobilization. Concern that training activities potentially generate environmental contamination in the form of residual munitions constituents has threatened range sustainment. The state of knowledge concerning the nature, extent, and fate of residual munitions constituents is inadequate to ensure environmental stewardship on testing and training ranges. These issues must be addressed if we are to continue range use while maintaining environmental protection. Project CP1155 was designed to characterize the distribution and fate of energetic residuals from various uses of live-fire munitions testing and soldier training ranges.

Scope of Project CP1155

This project was designed to develop techniques for assessing the potential for environmental contamination from energetic materials on testing and training ranges. Techniques are being developed to define the physical and chemical properties, concentration, and distribution of energetics and residues of energetics in soils, and the potential for transport of these materials to groundwater. Other issues, such as off-site transport in surface runoff, or as a component of airborne dust, are also important, but are beyond the scope of the project.

Surface soils associated with impact craters, targets areas, and firing points have been characterized on U. S. and Canadian ranges (Figure 1-1). Residues from high-order, low-order, unconfined charge, and blow-in-place detonations have been collected on witness plates, snow, and/or tarps. Analyses of these residues define concentrations and spatial distributions of munitions constituents under various firing activities for specific munitions. Special emphasis has been placed on developing sampling strategies for constituent residues. Transport parameters (desorption kinetics, partitioning coefficients, and transformation and/or degradation rates) for munitions constituents were determined using field soils from the sites as well as laboratory-spiked soils. The site-specific parameters were related to soil properties and compared to values at other sites. Transport parameters of contaminants of potential concern for which data are lacking

were determined by leveraging SERDP funds with other funding sources. Long-term fate and transport of explosives from cracked shells resulting from sympathetic detonations were investigated using large-scale lysimeters.

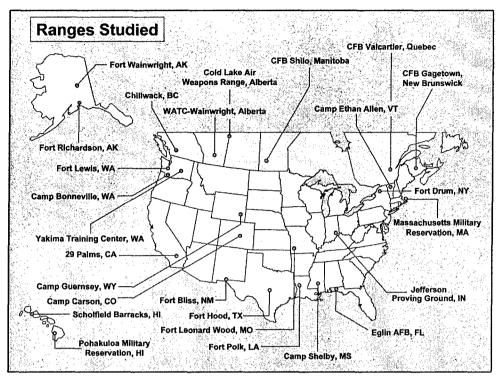


Figure 1-1. Installations where characterization testing has been conducted.

Tests were conducted to reliably generate low-order detonations. Residues from such blasts were assayed to develop a source term for use in fate and transport models and risk assessment models. The source term details the mass of explosive residue and, when appropriate, its areal and particle size distribution.

As additional sites are characterized, the database is expanded to determine whether certain munitions consistently contribute more contamination than others. Pertinent data from the Massachusetts Military Reservation (MMR) is reviewed and compared to the database annually to determine whether MMR residues are typical of other installations.

Objectives

The primary objective of the study is to provide the DoD with techniques to assess the potential for groundwater contamination from residues of energetic compounds (TNT, PETN, RDX, NG, 2,4-DNT, and HMX) at testing and training ranges. The results of the project will facilitate informed decision-making, help to minimize environmental impacts of testing and training, and contribute to continued operation of ranges.

Specific objectives include the following:

- To develop a protocol that can be used to determine the nature and extent
 of surface soil contamination around impact areas and firing points. The
 protocol will include sampling strategies and analytical methods best
 suited to this application.
- To provide source-term estimates of post-blast residues based on the extent of surface soil contamination, dissolution rates, and fate and transport process descriptors.
- To provide data describing the relevant environmental processes controlling the fate and transport of residues of energetic compounds on ranges.

Related Ongoing and Leveraged Studies

To meet the challenge of sustained training while protecting groundwater and other environmentally sensitive receptors, the U.S. Department of Defense (DoD) is funding a broad spectrum of research and development efforts. These efforts are funded under multiple programs and through many installations and address various aspects of range sustainability. Examples of programs funding research and development efforts related to range sustainment and environmental stewardship are the following. Our collaboration and leveraging of these projects is indicated where appropriate.

Strategic Environmental Research and Development Program (SERDP) identifies, develops, and transitions environmental technologies that relate directly to defense mission accomplishment. SERDP is the DoD's corporate environmental research and development program, planned and executed in full partnership with the Department of Energy (DOE) and the Environmental Protection Agency (EPA), with participation by numerous other Federal and non-Federal organizations. The DoD's environmental concerns may be viewed in terms of operational and/or cost impacts to its primary mission of maintaining military readiness for national defense. SERDP strives to minimize or remove major negative environmental impacts on DoD's ability to conduct this mission. SERDP has supported an extensive program of research related to range sustainment. SERDP projects with which we have collaborated and/or coordinated are described below.

- a. Compliance Project (CP) 1197, "A Field Program to Identify Toxic Release Inventory Chemicals and Determine Emission Factors from DoD Munitions Activities" (Chet Spicer, Battelle Columbus). The objective of the project is to demonstrate a methodology for measuring emissions of toxic release inventory (TRI) chemicals from DoD munitions activities and to apply the method to determine emission factors from munitions activities at DoD facilities. Results of tests to date in large chambers revealed the presence of nitroglycerin and dinitrotoluenes as well as dinitrobenzenes and dinitrophenols.
- b. CP1305, "Impacts of Fire Ecology Range Management (FERM) on the Fate and Transport of Energetic Materials on Testing and Training Ranges" (Eric Foote, Battelle Columbus). When this project was granted access to an Eglin

AFB range, we were invited to conduct the initial soil characterization and share the data with both projects. Therefore, we used protocols developed in CP1155 to sample surface soils on the range that is currently being used to determine the impacts of prescribed burning on residual energetics.

- c. CP1330, "On-Range Treatment of Ordnance Debris and Bulk Energetics Resulting from Low-Order Detonations" (Phil Thorne, Applied Research Associates, Inc.). The objective of this project is to develop a low-cost, fieldable process for the rapid decontamination of energetic material from range scrap. We have provided debris from low-order detonation tests at Blossom Point, MD, to facilitate trials of the techniques under development.
- d. CP1159, "A Predictive Capability for the Source Terms of Residual Energetic Materials from Burning and/or Detonation Activities" (Charles Kolb, Aerodyne). The objectives of this project are to define and model gaseous and particulate species formed by detonations. We have followed the progress of this project since it is directly relevant to the ultimate development of the potential source term of energetic residues on ranges. Results reported at the 2004 SERDP Symposium indicated that propellant residues and their combustion products predominate in the particulate emissions and that ablated metal alloys from the munition casing were also detected.

Defence Research and Development Canada - Valcartier (DRDC-Valcartier). The Director Land Environment (DLE) from the Canadian Head Quarters has tasked DRDC-Valcartier scientists to perform research characterization of their main army training areas to assess the impacts of live-fire training. Part of the work conducted within CP1155 is strongly linked with this objective. CP1155 includes partial funding for CFB Shilo and Gagetown and for Cold Lake Air Weapons Range for surface characterization, while the hydrogeological portion of these studies is supported by DLE. Moreover, the DLE mandate includes the analysis of other types of range contaminants, such as heavy metals, petroleum products, and radioactive compounds when appropriate. Just as data generated on U.S. ranges under CP1155 are shared with DRDC-Valcartier, so also are all of the data generated for Canadian studies of these other analytes shared with the U.S. The DLE mandate included other training areas, such as the one located at CFB Valcartier, and results obtained at this training area will be added to the CP1155 database. Future work at other Canadian training areas, such as Petawawa or Suffield, will still be supported partly by DLE. In FY2003, Canadian studies leveraged with SERDP funds also included "Explosives Residues Resulting from the Detonation of Unconfined Explosives Charges," and "Study of the Environmental Impacts of the Blow-in-Place Procedure of Various Explosives, Munitions and Charges." On a yearly basis, approximately 30 percent of the fund is contributed by the SERDP project. Finally, another directorate, Directorate General Environment (DGE), sponsors DRDC-Valcartier for a smallscale UXO corrosion study. The scientific leader of this study has met with the Principal Investigator of SERDP CP1226 to discuss the data that will be acquired and link the studies. DGE also sponsors work on the ecotoxicological properties of explosives, work that is closely linked with CP1155.

Army Environmental Quality Technology Program Focus Area on Characterization, Evaluation, and Remediation of Distributed Sources

- (UXO-C) on Army Ranges. This program, initiated in FY2003 contains 25–30 work units, several of which are related to project CP1155. The following work units are specifically relevant:
- a. Large-scale characterization of major contamination sources on military training ranges (Tom Jenkins, ERDC-CRREL). The objective of this work unit is to develop methods at the landscape scale for determining the types, numbers, physical dimensions, and distributions of large point sources of energetic compounds at various types of ranges.
- b. Minimization of explosive residues in blow-in-place procedures (Judy Pennington, ERDC-EL). The objective of this work unit is to optimize blow-in-place procedures while minimizing constituent contamination without compromising effectiveness and implementation ease. This project, conducted in coordination with the CE Huntsville and conducted at Redstone Arsenal, is heavily leveraged with CP1155.
- c. Range and landscape level characterization methodology (Rose Kress, ERDC-EL). The objective of this work unit is to develop geospatial methods for predicting patterns of contaminant distribution at the landscape level.
- d. Surface runoff of distributed source contaminants from soils: A laboratory simulation study (Cynthia Price, ERDC-EL). The objectives of this work unit are to describe movement of residues into the overland flow plane during rainfall/runoff events, to define stream routing relationships in surface runoff, and to develop soil infiltration and runoff extraction coefficients for modeling mass loading to surface water and groundwater.
- e. Development of a distributed source contaminant transport model for the Army Risk Assessment Model (ARAMS, Billy Johnson, ERDC-CHL). The objective of this work unit is to develop a model to simulate transport in the watersheds, rivers, streams, and groundwater linking a GIS interface and best management plans to ARAMS.
- f. Transport of explosives residues through the vadose zone (Judy Pennington, ERDC-EL). The objective of this work unit is to describe transport of RDX from solid explosives compositions on the soil surface through dissolution, degradation, and transport by developing process descriptors suitable for use in groundwater and transport models.
- U.S. Army Alaska Directorate of Public Works. The U.S. Army Engineer Research and Development Center (ERDC) Cold Regions Research and Engineering Laboratory (CRREL) is working for the U.S. Army Alaska Directorate of Public Works at Ft. Richardson and the Donnelly Training Area (formerly Ft. Greely). This work is an outcome of the environmental impact statement (EIS) in support of the renewal of the lease of land from the public domain under the Military Lands Withdrawal Act (Public Law 106-65). As a portion of this EIS the Army has pledged to implement a program to identify possible munitions contamination and evaluate the potential for surface water and groundwater contamination. In FY2003, sampling experiments were conducted at firing points within the Donnelly Training Area to evaluate various options for collecting

representative samples in areas where 105-mm howitzers were fired using single-based propellants. These samples were also utilized to compare various subsampling methods to maintain representativeness through the subsampling step of the analysis.

U.S. Army Environmental Center (AEC) Range Sustainment Program. The Army Environmental Center (John Buck), with the Center for Health Protection and Preventive Medicine (CHPPM, Barrett Borry), is also conducting a "Range Sustainment Program" to proactively ensure sustained training on ranges and to protect drinking water sources on active ranges. Project CP1155 is coordinated with this project and has shared site access with this project whenever possible to benefit both efforts. In FY2004, AEC extended joint access to us at Jefferson Proving Ground, IN, and Fort Polk, LA.

UXO in marine environments. The Naval Facilities Engineering Service Center, Port Hueneme, CA, and the Space and Naval Warfare Systems Center, San Diego, CA, are conducting a study in conjunction with the ERDC Environmental Laboratory to determine toxicological and geochemical interactions of ordnance and explosives in marine environments. Geochemical studies will determine dissolution, adsorption, and transformation rates of explosives in saline systems. Process descriptors determined in fresh water will be compared with those determined in salt water to determine what descriptors are affected by salinity. The toxicology studies will focus on toxicity, bioaccumulation, trophic transfer, and tissue concentrations of explosives in marine organisms, and the toxic effects of mixtures of explosives.

Summary of Results Through 2003

Since its inception in 2000, the study has developed an extensive database of energetic compounds in surface soils on training ranges. Strides have been made in documenting explosive and propellant residues on live-fire training ranges for various types of munitions. Identifying areas most likely to form distributed point sources of contamination and focusing sampling approaches on areas associated with specific aspects of training have been significant accomplishments. Environmental fate and transport process descriptors for specific explosive and propellant residues that are suitable for use in groundwater transport and risk assessment models have also been generated.

In FY2003 emphasis was placed on optimizing sampling protocols and defining residues by conducting controlled detonation experiments, including high-order, low-order and blow-in-place detonations. Results confirmed that the potential for constituent residues in surface soils is munitions specific and related to weapon system performance (i.e., incidence of low-order detonations and UXO generation) and site-specific conditions (i.e., local weather and hydrogeology). Specific findings in FY2003 were the following:

Massachusetts Military Reservation. Among the several thousand soil and groundwater samples collected at MMR (Camp Edwards) in 2003, no new explosive compounds have been detected. The most frequently detected propellants,

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explosives, and pyrotechnics in soils were (in decreasing order of frequency) TNT and the ADNTs followed by "Other" (di-n-butyl phthalate, N-nitrosodi-phenylamine, white phosphorus), perchlorate, DNTs, and RDX. Perchlorate predominated in groundwater, followed by RDX, HMX, and ADNTs in decreasing order of frequency. As perchlorate emerged as a contaminant of concern, previously identified perchlorate plumes were mapped, and two new perchlorate plumes, for which the sources are uncertain, were identified.

U.S. Range Characterization. The collection and analysis of numerous composite surface samples from different military training ranges established the presence of TNT, RDX, HMX, NG, 2ADNT, 4ADNT, and 2,4DNT, either at the firing position or on the impact area. The measured concentrations can be used to estimate the mass available for dermal exposure, ingestion, and migration into surface and subsurface water systems. To overcome the compositional and distributional heterogeneity common to dispersed explosives particles, the use of composite sampling strategies is recommended. Processing of soil samples through a # 30 (0.6-mm) sieve as currently recommended in Method 8330 is not recommended because sieving to <2 mm prior to mechanical grinding removes compounds of interest and results in underestimation of concentrations.

Canadian Range Characterization: Gagetown. Sampling of surface soils at Gagetown artillery, anti-armor, antitank, grenade, and small arms ranges identified specific energetic materials related to the various activities. Artillery impact areas exhibited RDX, TNT, and amino-DNTs, while firing points exhibited relatively high levels of NG and low levels of 2,4DNT from propellants. Firing positions for anti-armor and antitank weapons yielded up to percent levels of NG and 2.4DNT from single- and double-based propellants. Impact points for these ranges had low concentrations of TNT and RDX. Firings of Octol-based M72 shoulder-launched antitank rockets generated residues of HMX in surface soils and HMX and TNT at several inches of soil depth. At grenade ranges, TNT, TNT derivatives, and RDX predominated. Detections of 2,4DNT and NG on the grenade ranges may be the result of unknown past use of the area or of burning of unused propellants. In general, explosive residues were detected at lower concentrations on artillery ranges than on anti-armor or antitank rocket ranges. Detection of explosives on these Gagetown ranges was typical of similar ranges investigated in Canada.

Surface soils were also sampled for heavy metals on Gagetown ranges. The results revealed concentrations of concern for cadmium, copper, lead, and zinc, especially at anti-armor and antitank ranges. Grenade ranges exhibited high concentrations of zinc, while small arms ranges exhibited high concentrations of copper and lead (lead up to 0.4 percent by weight). Concentrations of molybdenum, antimony, strontium, and chromium also exceeded background concentrations. Vegetation also exhibited significant concentrations of cadmium, lead, and zinc. Bioaccumulation of these metals is problematic because high concentrations of the salts of sodium, calcium, and potassium exist concurrently with the heavy metals. Grazing animals are then specifically attracted to the high salt content and preferentially feed on the contaminated vegetation. Typically, concentrations of heavy metals in the vegetation correlated with concentrations observed in the soils. Contamination by a mixture of explosives and heavy metals was observed on grenade and antitank ranges.

Canadian Range Characterization: Cold Lake. Results of explosives analyses of surface soil samples on the Cold Lake ranges illustrate the difference between residues from artillery ranges and those from air-to-ground ranges. Of the four ranges sampled, only one, Shaver Range, is used for training with HEcontaining munitions. This range exhibited high concentrations of explosives residue, predominantly TNT (up to 400 ppm). Other ranges exhibited low concentrations of TNT, RDX, and HMX. Concentrations tended to be localized around targets. One range, Jimmy Lake, had significant concentrations of propellants, especially NG. Detections of heavy metals on the four ranges were also limited. Notable detections included Cd, Cu, and Zn. The low metals concentrations were attributed to range maintenance practices by which metals are removed on a regular basis. Concentrations of metals in the vegetation were usually higher than in the soil. Since cadmium was a significant detection in vegetation, additional sampling was conducted in FY2004 (see Chapter 5 in this report). No explosives, propellants, and metals were detected in the surface water of the lakes.

Snow Tests for Residues from High-Order Detonations. Results of residue collection on snow following detonations of artillery projectiles, mortars, and hand grenades demonstrated that high-order detonations consume an average of 99.997 percent of the high explosive. The unconsumed residue is assumed to occur as fine particles, which would result in very low concentrations over a relatively large area. These results are consistent with results obtained by sampling ranges where these weapons have been fired repeatedly. The contribution of explosives residues from high-order detonations during live-fire training is concluded to be insignificant. Low-order detonations and blow-in-place demolition are the more likely sources of significant residues of high explosives.

Residues from Detonations of Unconfined Explosives. Detonation of unconfined charges represents a worst-case scenario by generating greater residues than would result when charges are confined by a metal case. When explosives are unconfined, detonation pressure is greatly reduced, detonation is consequently less efficient, and a greater quantity of residues is anticipated. This was demonstrated by detonation of explosives of various sizes and shapes. The results indicated that a relatively low percentage of explosives remained after detonation. Larger charges yielded smaller residues. Cylinders dispersed more TNT residue than other configurations of TNT; however, when the cylinder data were excluded, the overall maximum dispersion of TNT was only 0.2 percent. Dispersion of residual RDX tended to exceed residues of the other explosives, especially when the RDX source was C4 blocks. Two insensitive munitions, a plastic-bonded explosive (PBX) and XRT, yielded relatively high dispersion. The results of these studies demonstrate that, even without the pressure of confinement, explosives residues from high-order detonations are minimal.

Residues from Blow-in-Place Demolition. The results of blow-in-place detonations of various munitions demonstrated that the main charge was not always efficiently consumed. For low-order detonations, more residues (up to a few percent) were recovered independently of the configuration tested. High-order detonations were characterized by less residue than low-order detonations; the *maximum* values found were 1.0, 0.6, and 0.5 percent for TNT, RDX, and HMX, respectively. Such relatively high recoveries of residues compared to

those observed when the munitions are actually fired (see paragraph e above) illustrate a difference in performance between impact detonations after firing and blow-in-place detonations by an external donor charge. Typical levels from the high-order blow-in-place detonations were less than 0.1 percent for TNT, RDX, and HMX, which still exceeds residues observed from fired munitions. To ensure high-order detonations of 60- and 81-mm mortars, 150 g of C4 on the side of the casing is recommended. FIXOR and the commercial shaped charges of 16.5 and 36 g could also be used. All of the configurations of hand grenade detonations produced high-order detonations. For the landmine (PMA-1A), 4–30 g of C4 in a lateral hole or the use of FIXOR led to high-order detonations.

Environmental Fate and Transport Process Descriptors. To understand and anticipate the environmental fate and transport of energetic compounds, such as explosives and propellants, fundamental parameters such as solubility, dissolution rate, adsorption, transformation, and irreversible soil binding must be determined. For many of the energetic compounds encountered on ranges, these parameters were unknown. Therefore, emphasis was placed on filling such deficiencies with data based on laboratory determinations. In FY2003, fate and transport process parameters were determined for nitrobenzene, perchlorate, nitroguanidine, diphenylamine, *N*-nitrosodiphenylamine, and ethyl centralite. Nitrobenzene is an impurity in TNT and a potential photodegradation product. Perchlorate, nitroguanidine, diphenylamine, *N*-nitrosodiphenylamine, and ethyl centralite are propellant components that have been detected on firing ranges.

The solubilities of diphenylamine, N-nitrosodiphenylamine, and ethyl centralite were limited, ranging from approximately 10 to 50 mg L⁻¹ over a range in temperatures from 10 to 30 °C. Adsorption coefficients of all five compounds were typically less than 20 L kg⁻¹, suggesting limited attenuation by sorption mechanisms in the soil. However, nitrobenzene and diphenylamine were degraded in surface soils, although not in aquifer soils, while N-nitrosodiphenylamine was degraded in the aquifer and one of the surface soils. These compounds are, therefore, subject to degradation in the environment. Nitroguanidine and ethyl centralite were not degraded in any of the tested soils and, consequently, are expected to persist in the environment. Perchlorate, which was tested under a wide range of pH and redox conditions, was recalcitrant to degradation under all conditions, even when fresh soil inoculum was added to the tests.

General Conclusions. The following are the pertinent conclusion of the various investigations conducted through 2003.

- a. Munitions constituents emerging as the principal concern on impact areas of heavy artillery ranges include RDX, TNT, and HMX.
- b. Significant contamination has been observed at heavily used artillery firing points, where the principal constituents observed were NG and 2,4DNT. Perchlorate is a potential concern at firing points.
- c. Energetic material residues at both impact and firing points tend to exist as solid particles having the composition present in the munitions prior to firing. Therefore, the potential source contamination is heterogeneously distributed, highly heterogeneous in particle size, and often complex in chemical

composition. Characterization of such residues requires careful consideration of these properties of the source and careful consideration of sample representativeness during collection and during processing and analysis.

- d. Although various constituents present different characteristics, the most important fate and transport processes governing these residues tend to be dissolution and transformation rather than degradation or adsorption to soils. With the exception of TNT, which is often easily attenuated in the surface soils after transformation, explosives residues are relatively slow to dissolve but readily mobilized once in solution. Therefore, they present a concern for leaching to groundwater slowly over time.
- e. Range management practices designed to minimize low-order detonations and UXO generation, remove large observable masses of residues and UXOs, and minimize contamination in blow-in-place disposal will promote control of contamination while maintaining active range use.

The results of this study provide a technical basis for developing rangespecific soil characterization approaches and process descriptors for fate and transport of constituent residues and for assessing the exposure component of environmental risk assessments. The relationships emerging between various training activities and residues of energetics can form the basis for sound management of training ranges while maintaining environmental stewardship.

FY2004 Execution

The chapters in this report are extended abstracts that summarize the work conducted in FY2004. Some chapters stand alone, but for others a more comprehensive report containing the data is being published under separate cover by the agencies conducting the work. In those cases a reference to the annotated publication can be found at the beginning of the specific chapter.

Characterization of residues was conducted at the following ranges in FY2004: Jefferson Proving Ground, IN; Eglin Air Force Base, FL; Fort Polk, LA; Ft. Carson, CO; Ft. Hood, TX; 29 Palms, CA; CFB Gagetown, New Brunswick; and Cold Lake Air Weapon Range, Alberta. CFB Gagetown and Cold Lake Air Weapon Range were sampled in previous years of this study. CFB Gagetown was sampled again in FY2004 (Phase III) to delineate more precisely the extent of contamination by munition-related contaminants on specific ranges. For example, new patterns of sampling were studied that will allow a better statistical analysis of the dispersion of explosive in an antitank range. Cold Lake (Phase II) was revisited to confirm the results obtained in the first phase and delineate more precisely the extent of soil contamination. A third phase was also sponsored by Canadian DND to execute a groundwater monitoring program. Sample and data analyses for all of these sites are ongoing. This report includes data from Ft. Polk, LA; Gagetown Phase III; and Cold Lake Phase II. The results of more extensive sampling for metals on Canadian ranges are included in the Gagetown and Cold Lake chapters. The results of tests to determine residues from low-order detonations, sympathetic detonations, and blow-in-place procedures are also

reported here. An update of explosives-related sampling at the Massachusetts Military Reservation is also included.

Accomplishments to date of SERDP Project CP1155 include the following:

- a. Data acquisition for estimating firing range source terms for various munitions and range usages including high-order detonations, low-order detonations, and munitions firing points.
- b. Protocol for characterizing soil contamination on various types of ranges having high spatial and concentration variability, e.g., heavy artillery, antitank, hand grenade, and air fighter training.
- c. Definition of the residues generated by various UXO demolition procedures (blow-in-place).
- d. Process descriptors for range-specific energetic residues, including dissolution rates, partition coefficients, and transformation rates.

A bibliography of technical reports and presentations generated during execution of project CP1155 is included (Appendix A). Web sites where reports may be available include the following:

- CP1155 (http://www.wes.army.mil/el/serdp/index.html)
- ERDC EL (http://www.wes.army.mil/el/t2info.html)
- ERDC CRREL (http://www.crrel.usace.army.mil/products/products.html)
- Défense R & D Canada-Valcartier (http://www.valcartier.drdc-rddc.gc. ca)
- MMR Impact Area Groundwater Study (http://www.groundwaterprogram.org/index.html and http://www.mmr-edms.net).

Format of this Report

The chapters in this report represent expanded abstracts of the research conducted in FY2004 on each topic. Chapters 2, 4, and 5 are abstracted from government reports already published as cited at the beginning of each of these chapters. Other chapters represent progress in FY2004 that may be developed into other reports or articles in technical journals once FY2005 data from this and/or other ongoing projects are added.

Appendix A: Bibliography of CP1155 Publications

Refereed Journal Articles:

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Chapter 1 Introduction 21

2 Sampling Strategies Near a Low-Order Detonation and a Target at an Artillery Impact Area

The information appearing in this chapter is also published in the following government technical report:

Jenkins, T. F., Hewitt, A. D., Ranney, T. A., Ramsey, C. A., Lambert, D. J., Bjella, K. L., and Perron, N. M. (2004). "Sampling strategies near a low-order detonation and a target at an artillery impact area," ERDC/CRREL TR-04-14, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, NH.

Introduction

Several recent papers have reported on the difficulty in collecting soil samples representative of the mean analyte concentrations on military training ranges in areas where energetic residues accumulate (Ampleman et al. 2003a, b; Jenkins et al. 1996, 1997, 1999, 2001, 2004; Pennington et al. 2001, 2002, 2003; Thiboutot et al. 1998, 2003; Walsh et al. 2001, 2004). This difficulty is because energetic residues generally are distributed heterogeneously as particles on the surface. Because such particulate residues serve as the major source of potential off-site migration of these compounds, it can be important to estimate the mass of energetic materials in areas where they are present. Establishing the mass of energetic residues within a decision unit is a practical way of dealing with areas that contain both particles and chunks of neat material. To achieve more reliable estimates of the mean residue concentration for calculating the mass, multi-increment sampling strategies and larger surface soil sample masses than have traditionally been collected for environmental investigations are being evaluated.

Objectives

Sampling experiments were conducted in an active mortar and artillery impact range to determine the best sampling strategy for collecting representative

surface soil samples to estimate mean concentrations of residues of high explosives. In addition, sampling was performed to determine the pattern of energetic residues around a target receiving indirect fire. Two types of potential accumulation zones for energetic residues were sampled: (1) the area around a partial detonation of an 81-mm mortar and (2) the area around an artillery/mortar target. Discrete and multi-increment composite soil samples were collected in the vicinity of the low-order detonation to assess the surface mass loading of energetic residues and investigate the spatial distribution of surface soil concentrations within the impacted area. Multi-increment samples were collected around the artillery target to enable estimation of the mass loading in this area and to determine if there was a concentration gradient near the target, as has been found at antitank rocket range targets (Jenkins et al. 1997, 1998, 2004).

Field Site

This study was conducted on an impact range at Fort Polk, Louisiana, from 25 to 29 June 2003. One location was chosen after finding what appeared to be chunks of explosives residue on the soil surface (Figure 2-1). Upon analysis, these chunks were found to be composed of TNT and RDX (Composition B: 39 percent TNT, 60 percent RDX). The presence of a fin and a casing fragment indicated that the explosives residues originated from an 81-mm mortar that had undergone a low-order detonation. The second location selected for sampling was a heavily impacted artillery target approximately 30 m uphill from where the small chunks of explosives residues were found.



Figure 2-1. Chunks of Composition B from the partial detonation of an 81-mm mortar round found in the artillery impact area at Fort Polk, Louisiana.

Methods

A $10-\times 10$ -m sampling area, further subdivided into $100\ 1$ -m² grids, was positioned to encompass the visible chunks of energetic residue. Around this sampling area, 10-m linear transects were also established parallel to all four sides at distances of 2, 5, and 10 m (Figure 2-2, Area A). The area around the target, uphill from the $10-\times 10$ -m area, was divided into twelve sampling grids. The grid boundary extended 2 and 5 m from the edge of the target (Figure 2-2, Area B).

Prior to collecting discrete and multi-increment composite samples within the 10- × 10-m grid surrounding the low-order 81-mm mortar, we marked and recorded the location and weight of each chunk of energetic residue visible on the surface. A single discrete sample (50-100 g) was then obtained from each of the 100 1-m² grids. Subsequently, for twenty randomly chosen 1-m² grids, a second co-located discrete sample was collected along with a 10-increment composite sample (800 g). When a chunk of explosive was present within a 1-m² grid (if more than one, the largest chunk), the discrete sample was collected adjacent to the position where it was found. In addition, ten replicate, 25-increment composite samples (2 kg) were collected within the 10- × 10-m area using a random sampling strategy. Along the linear transects and within the grids located around the target, 10-increment composite samples were collected. All of the composite samples, with the exception of 10-increment composites collected along linear transects, were collected using a random sampling strategy. All discrete samples and composite sample increments were obtained with a coring device (4.8 cm in diameter, 2.5 cm deep) (Walsh 2004).

Soil samples were returned to CRREL and air-dried at room temperature. Discrete and composite samples were weighed and passed through a #10 (2-mm) sieve to remove oversized material (pebbles, sticks, etc.). The sieved portions were weighed and returned to their respective containers. A volume of acetonitrile, approximately double the mass of the sample, was added to the discrete samples. The samples were placed on a rotary tabletop shaker overnight (18 hours) for extraction. Because the multi-increment samples were much larger than the discrete samples, these samples were subsampled as follows. All of the material in each of the multi-increment composite samples that passed through the sieve was ground in a LabTech Essa LM2 (LabTech Essa Pty. Ltd., Bassendean, WA, Australia) puck mill for 60 seconds. After grinding, each composite sample was mixed thoroughly and subsampled. A mass of 10 g was extracted with 20 mL of acetonitrile in an ultrasonic bath overnight at room temperature. Walsh et al. (in prep) has determined that the shaker table and sonic bath extraction are equivalent for most soils.

The extracts from the discrete and composite samples were analyzed using the general procedures outlined in SW846 Method 8330 (EPA 1994). For low-concentration samples, a second analysis was conducted by GC-ECD following the general procedure outlined in SW846 Method 8095 (EPA 1999).

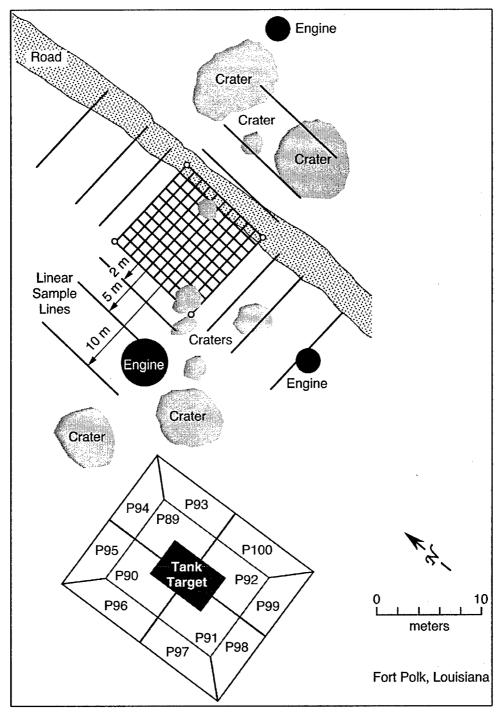


Figure 2-2. Sampling grids around a tank target in the artillery impact area at Fort Polk, Louisiana.

Results

Samples Collected near Chunks of Energetic Residues

RDX, HMX, TNT, 2ADNT, and 4ADNT were detected in nearly all of the discrete surface soil samples for the 100 1-m² grids. RDX was present at the highest concentrations, with surface soil concentrations ranging over almost five orders of magnitude (0.037 to 2,390 mg/kg) (Table 2-1). The median RDX concentration was 1.79 mg/kg, but the presence of several very high concentrations elevated the mean concentration to 70.9 mg/kg, indicating a non-normal distribution. HMX concentrations in these 1-m² grid samples ranged from less than our detection limits (0.01 mg/kg) to 253 mg/kg. The ratio of the HMX mean concentration to the RDX mean concentration was 0.195, which is slightly higher than expected based on the analysis of the chunk residue from this site, where the HMX/RDX ratio was 0.11 (HMX is an impurity in the manufacturing of RDX). This ratio suggests that weathering has resulted in the preferential dissolution of the more-soluble RDX.

Table 2-1 Summary of Results for Discrete Samples from 100 1-m ² Grids (mg/kg)												
	НМХ	RDX	TNT	4ADNT	2ADNT							
Max	253	2390	1560	16.3	15.3							
Min	0.005	0.037	0.001	0.008	0.008							
Median	0.395	1.79	0.044	0.120	0.169							
Mean	7.89	70.9	29.7	0.626	0.669							

TNT concentrations in these samples were always lower than RDX and ranged from less than 0.002 mg/kg to 1,560 mg/kg (Table 2-1). The ratio of the TNT mean concentration to the RDX mean concentration was 0.107. For non-weathered Composition B, the ratio should be about 0.65, indicating that the TNT present in these samples has been subject to preferential dissolution and environmental transformation. The two most common environmental transformation products of TNT—2ADNT and 4ADNT—were detected in all 100 1-m² grid samples, even in samples where the TNT concentration was below the detection limits. The median ratio of 2ADNT to 4ADNT was 1.18; this ratio is typical for these compounds in surface soil samples (Jenkins et al. 2001).

The distribution of RDX in the 100 discrete 1-m² grid samples was non-Gaussian (Figure 2-3). A plot of the RDX concentrations in surface soil versus position within the 10- × 10-m area indicated that two locations had much higher concentrations, indicating potential hot spots within this decision unit. One was centered near the lower edge, and another smaller one was near the left edge (Figure 2-4). We define hot spots to be areas where the soil concentrations were greater than 100 mg/kg. These apparent hot spots correspond closely to the mass of chunks of Composition B recovered from the individual 1-m² grids (Figure 2-4).

The results for the duplicate discrete samples from the 20 randomly selected 1-m² grids show that agreement between replicates is analyte dependent. For example, while the difference between the RDX, TNT, and HMX concentrations for the field duplicates was often greater than an order of magnitude, the discrepancy between 4ADNT and 2ADNT was often less than a factor of three. This anomaly can be explained by the physical state of these analytes. RDX, TNT, and HMX are present as crystalline particulates, whereas 4ADNT and 2ADNT are formed only following dissolution and subsequent transformation. Therefore, one group of energetic materials exists predominantly as discrete particles, while the other exists on the surfaces of soil grains after adsorption from the pore water. The results for the 10-increment composite samples collected within the same randomly selected mini-grids where duplicate discrete samples were collected exhibit the same trends as for the field duplicate discrete samples.

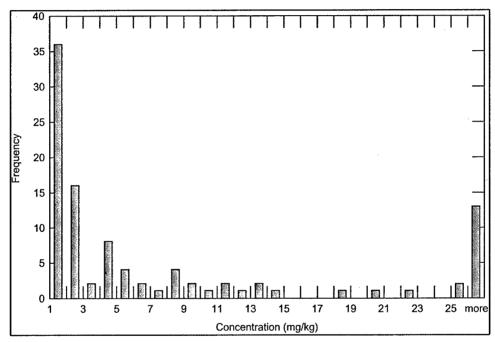


Figure 2-3. Distribution of RDX concentrations from 100 discrete soil samples. Note: "more" is used to denote discrete samples with concentrations greater than 25 mg/kg.

The ten random 25-increment composite samples collected within the entire $10-\times 10$ -m area showed minimum and maximum concentrations for RDX of 4.62 and 294 mg/kg, respectively. Recent results from sampling at Canadian Force Base–Gagetown (Thiboutot et al. 2004) showed that systematically collected multi-increment composite samples could provide more reproducible results within a confined area of concern than composite samples collected using a random sampling strategy. We evaluated this theory by creating four mathematically systematic composite samples (n = 25) by combining every fourth discrete sample from the 100 discrete 1-m² grids. A comparison of the results for the 100 discrete samples, the ten randomly collected 25-increment composites, and the four systematic mathematical 25-increment composites is shown in Table 2-2. The range of RDX values is much reduced, from a factor of about 10^5 for the

discrete samples to factors of 64 and 3, respectively, for the randomly and systematically collected composites.

Table 2-2
Comparison of Concentration Estimates for Target Analytes using
Various Collection Strategies in a 10- x 10-m Grid near a Low-Order
Detonation

	Increments per	Number of	Analytes (mg/kg)					
Collection Strategy	Sample	Replicates	RDX	НМХ	TNT			
Discrete samples	1	100						
Max			2390	253	1560			
Min			0.037	0.005	0.001			
Mean			70.9	7.89	29.7			
Median			1.79	0.395	0.044			
% RSD*			444%	415%	529%			
Composite (random)	25	10						
Max			294	32	106			
Min			4.62	0.594	0.752			
Mean			54.6	5.99	17.7			
Median			24.5	2.93	5.17			
% RSD*			159%	157%	179%			
Composite (systematic)	25	4						
Max			99.8	10.8	63.2			
Min			33.1	3.81	10.3			
Mean			70.9†	7.89†	29.7†			
Median			75.3	8.46	22.7			
% RSD			43.3%	40.0%	77.8%			

^{*} When the RSD is greater than 100 percent the data are not normally distributed and it is not possible to compute useful limits of uncertainty.

Comparing the median value obtained from the 100 discrete samples with those from the ten 25-increment random and the four 25-increment systematic composite samples is interesting, because half of the samples collected will have concentrations below these median values for this decision unit. The median of the discrete samples for RDX was 1.79 mg/kg, the median for the ten composite samples was 24.5 mg/kg, and the median for the four systematic samples was 75.3 mg/kg. Thus, rather than diluting out the high concentrations, the multiincrement composite samples are more likely to capture the high concentrations that would generally be missed if only a limited number of discrete samples were collected. The mass of energetic residues within this 10- × 10-m decision unit would therefore be grossly underestimated in most cases if they were based on the concentration estimated for a single or several discrete samples. The concentration of RDX with this area based on the weighted average of the 100 1-m² discrete samples and the 10 25-increment samples is 59 mg/kg. The medians for the two modes of collecting multi-increment samples are within a factor of two of this concentration, whereas more than half of the time a single discrete sample would at least an order of magnitude lower. Based on the weighted average concentration, a sampling depth of 2.5 cm, and a soil density of 1.7 g/cm³, the

[†] Values are the same as the 100 discrete samples since the same data set was used.

estimated mass of RDX in the soil in this decision unit is 250 g. This is about twice the mass of RDX established for the chunks of Composition B found on the surface

	Ma	ss of C	ompo	sition I	B (g) (Collecte	ed in (3rid			RD	X Cor	centra	ation ir	3 Surfa	ace So	il (mg/	/kg)	
	·									17.1	1.27	0.829	0.908	10.9	4.44	0.437	0.354	1.52	0.067
										0.805	24.1	7.73	0.539	0.260	0.233	0.366	1.93	0.731	0.138
										30.8	1.40	12.5	0.342	0.074	1.11	0.18	0.076	7.11	0.187
	1,1	0.9	4.5	1.2	0.1					12.7	138	53.7	3.85	4.94	1.22	4.63	0.470	2.41	1.06
0.2		16.3					•			331	9.70	3.96	1.44	3.67	0.243	3.21	0.254	1.03	0.073
			0.1	0.1						7.52	5.65	1.97	0.571	4.84	19.9	0.825	0.122	1.46	0.070
0.4						-				1.65	1.56	8.51	10.6	2.24	25.2	7.15	0.248	0.175	0.037
1.4	0.2		3.0	48.2	13,1	1,0	0.4			48.3	13.3	3.36	6.93	889	21.8	3.75	0.618	0.193	0.081
		26.1	7.8	5,5	17.9	0.3				1.18	1.03	64.3	557	1790	2390	11.3	1.65	0.335	0.263
	0.1	50.2	0.1	0.1		0.3				8.86	3.50	5.02	42.7	385	24.9	3.64	0.96	0.526	0.161
1	2	3	4	5	6	7	8	9	10	1	2	3	4	5	6	7	8	9	10
										k, Louisian id (10 m x									

Figure 2-4. Weights of Composition B chunks and soil RDX concentrations relative to position in the sampling grid. Areas shaded either contained more than 1.0 g of Composition B or had an RDX soil concentration greater than 100 mg/kg.

Samples collected near a mortar/artillery target

The 10-increment composite surface soil samples that we collected near an artillery target showed concentrations of RDX that varied from 0.106 to 15.9 mg/kg. However, unlike HMX concentrations near an antitank target (Jenkins et al. 1997, 1998, 2004), no concentration gradient relative to distance from the target was observed. TNT concentrations in these samples varied from 0.076 to 18.8 mg/kg, and the ratios of TNT to RDX were often higher than the 0.65 ratio expected from the deposition of fresh Composition B. Most 155-mm artillery rounds are filled with TNT rather than Composition B. Judging from the ratio of TNT to RDX, a portion of the explosives residues detected near this target was from TNT-filled rounds. The ratio of HMX to RDX in these samples was also often higher than found in and near the 10- × 10-m area located downhill and to the right of this target. This implies that the Composition B residues near this target are somewhat older (i.e., more weathered) than those near the low-order 81-mm mortar round.

Summary and Conclusions

Surface soil samples from an artillery/mortar impact area located at Fort Polk, Louisiana, were collected and analyzed for explosives residues. Two distinct areas were selected for sampling. The first was around a low-order detonation event, and the second was around a tank target.

The first sampling area was selected because numerous pieces of Composition B residue were lying on the soil surface, providing an opportunity to evaluate sampling strategies for a decision unit that included a potential "hot spot." A $10\text{-}\times10\text{-}\text{m}$ sampling area that encompassed the residue chunks of Composition B was further subdivided into $100\ 1\text{-}\text{m}^2$ grids. Among the $1\text{-}\text{m}^2$ grid discrete samples RDX ranged in concentration over approximately five orders of magnitude. Likewise, TNT concentrations ranged from below the detection limit $(0.002\ \text{mg/kg})$ to $1560\ \text{mg/kg}$, or more than six orders of magnitude. Field duplicate discrete samples were collected from 20 randomly chosen $1\text{-}\text{m}^2$ grids. The differences between these field duplicates varied by up to three orders of magnitude, indicating that single samples cannot represent areas as small as one $1\text{-}\text{m}^2$ grid for energetic materials that exist as particulates.

Ten composite samples of 25 randomly chosen increments each were taken over the entire 10- × 10-m area. The median RDX concentration for the ten 25-increment composite samples was fourteen times higher than the median of the 100 discrete samples. Also, RDX concentrations for these composite samples varied by as much as a factor of 60 as a result of the number of times the hot spot was sampled. Therefore, under these conditions, an unacceptable level of uncertainty remains among composite samples composed of 25 randomly collected increments, even though there was a large improvement over discrete sampling.

Mathematically generated systematic samples were created by "compositing" from the 100 discrete samples data, using every fourth 1-m² grid value. This was performed four times, thereby using all of the 1-m² grid samples. The median value for RDX was three times greater than the 10 random composites median and 42 times the median for the discrete samples. The RDX concentration range for the results of these four systematic mathematical composites was 33 to 100 mg/kg, whereas the range was 5 to 294 mg/kg, and 0.04 to 2,390 mg/kg for the ten 25-increment randomly collected composites and the 100 discrete samples, respectively. Therefore, the systematic approach is more likely to consistently capture hot spots of the sizes encountered in this study.

Overall, it is important to understand the nature of the distribution of energetic residues when designing a sampling strategy to establish an average concentration for a decision unit. The presence of a hot spot within the decision unit is a worst-case scenario that confounds sampling uncertainty. Both types of composite sampling strategies generated estimates of the mean concentration for mass loading calculations for this type of area that are more reproducible and more accurate than a discrete sample. Additional studies are planned to compare the results obtained for systematically versus randomly collected multi-increment for different areas where energetic residues accumulate on firing ranges.

At the second area chosen for sampling, a sampling design and strategy was used to delineate if there was a gradient of energetic residue concentrations around the target receiving indirect fire. RDX concentrations varied from 0.1 to 16 mg/kg within the chosen sampling areas, with no apparent pattern to the distribution of RDX. Therefore, targets receiving indirect fire do not appear to have a concentration gradient moving out from the target, such as those found around targets at antitank ranges, where line-of-sight training is performed.

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3 Explosive Residues from Low-Order Detonations of Artillery Munitions

Introduction

Background

Residues from low-order detonations, i.e., munitions that explode incompletely leaving scattered high-explosive compositions on the soil surface, are a potentially significant point source of environmental contamination on training ranges (Pennington et al. 2001, 2002, 2003, 2004). Currently, no means has been developed for estimating the mass of residual explosive resulting from low-order detonations. Therefore, these studies were conducted to characterize the nature and quantity of residues from low-order detonations of selected artillery munitions.

The intentional creation of low-order detonations has special application in the explosive ordnance disposal (EOD) community when neutralizing ordnance. Neutralizing munitions requires consideration for the safety of personnel and the integrity of nearby assets. To maximize safety and reduce hazards, a method to neutralize the munitions without releasing their maximum energy is desired. During a previous NAVEODTECHDIV effort, the main charge disrupter (MCD) was developed as a technique for producing low-order detonations to reduce the hazard of removing such munitions. Testing was performed with MCD tool candidates against projectile munitions in June 1997 (Baker et al. 1997). During 1998 and 1999, Developmental Testing, Phase IIA involved testing the selected MCD tool candidate against MK 80 series and penetrator bombs (Blankenbiller 1999). Additional testing was performed in November 1999 with the MCD tool against additional MK 80 series bombs. In May 2000, the MCD tool was tested against a variety of unexploded ordnance (UXO) at Nellis Air Force Base and Fallon Naval Air Station. The explosive fills of the UXO included Tritonal, PBXN-109, Composition H-6, and Composition B. Various yields were achieved with the MCD by varying its placement and explosive loading. Hence, the MCD was chosen for the low-order chemical release (LOCR) series of testing to provide controlled yields for low-order detonations.

The following are typical situations in which low-order detonations occur:

- The explosive train (fuze, booster, or main charge) of a fired round can malfunction.
- A piece of UXO can be low-ordered (a secondary detonation) as a result of a fragment impact from a high-order detonation (primary detonation).
- EOD personnel can create a low-order detonation intentionally for the express purpose of neutralization (the purpose for the development of the MCD tool).

In a low-order detonation, consumption of the explosive filler is less than 100 percent. A low-order detonation is typically characterized by increased burn time, increased light intensity, reduced blast pressure, reduced impulse, and the presence of unreacted residual explosive (i.e., explosive that was not consumed during the detonation nor burned afterwards in the fireball). Explosive that has reacted or was consumed later during the low-order process (i.e., not during the detonation) is usually consumed through combustion. Any unreacted explosive may or may not be ejected from the round (Figure 3-1). Unreacted explosive can also be melted and released to the surrounding environment as a result of the heat from the reaction. The amount of unreacted residual explosive is likely to be a function of the energy yield of the detonation, the overall size of the detonation, and the intensity and burn time of the fireball.



Figure 3-1. Typical low-order detonations. a. Casing and residual Composition B ejected from a 60-mm mortar, b. Casing and residual Composition B retained in a 60-mm mortar, c. Casing and residual TNT ejected from a 105-mm projectile, d. Casing and residual TNT retained in a 105-mm projectile

Objectives

Specific objectives were (1) to determine the relationship between the mass of residues and the distance from the detonation center; (2) to determine the particle size distribution of residues, (3) to relate the residue mass to overpressure, a measurable characteristic of the blast, and (4) to determine whether detonations have a directional component related to the placement of the secondary charge or detonation tool.

Materials and Methods

Detonations

Low-order detonations of artillery munitions were achieved using the following two EOD tools: the MK 2 MOD 1 shaped charge, and the main charge disrupter (MCD). Munitions tested (Nomenclature, type, and quantity of fill) included the following: 60-mm mortars (M720, Composition B, 190 g), 105-mm projectiles (M1, Composition B, 2.3 kg), and 155-mm projectiles (M107, TNT, 6.6 kg). The MK 2 MOD 1 shaped charge consists of a 32-mm (length) by 25-mm (diameter) sheet metal tube with a 90° conical metal plate attached to one end. The tool was loaded with 15-17 g of C-4 explosives to produce a highvelocity jet (approximately 13,800 feet per second, or 15,139 km per hour) when initiated. The MCD consists of an aluminum cylinder 13 cm long by 4.62 cm in diameter containing a convex, copper liner in one end (Figure 3-2). The velocity of the MCD is altered by varying the explosive load (typically 57–170 g of C-4) and the number of nylon attenuators placed behind the copper liner. The typical MCD projectile velocity is approximately 6,000 feet per second. An RP-83 exploding bridge wire detonator (Reynolds Industries Systems Incorporated, San Ramon, CA) was used to initiate all of the EOD tools.

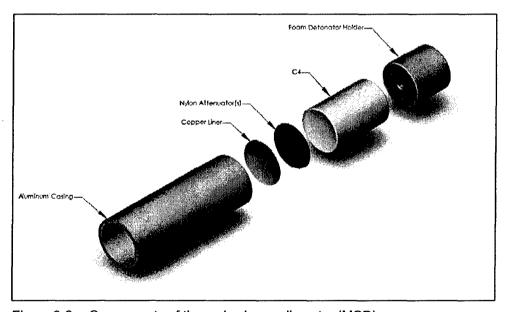


Figure 3-2. Components of the main charge disrupter (MCD).

Both EOD tools produce projectiles that can initiate an energetic reaction within the explosive filler upon impact or penetration. The selection of the tool was based on the size of the munition to be detonated. The standoff distance, the angle of the tool relative to the munition, and the impact point on the casing can be varied to achieve specific over-pressure levels, or energy yields, from the detonations. Several configurations of steel stands were used to support the position of the tool relative to the munition, which was positioned with the fuze end pointing upward.

The tests were conducted on a square raised table (approximately 1.52 m^2) of 3.81-cm steel (Figure 3-3). The table was supported by stacked $6\text{-}\times6\text{-inch}$ ($15\text{-}\times15\text{-cm}$) timbers to create a square perimeter 200.67 cm on each side. The overall elevation of the tests was 76.2 cm. Four solid steel cylindrical columns, 15.24 cm in diameter and approximately 1 m tall, were supported by angled braces welded to the table at the center of each side. These columns were used to protect pressure gauges from fragments created during the detonations. For the smaller munitions an additional set of four 3.81-cm-diameter steel poles were threaded into a welded flange near the corners of the table. These were used when the pressure gauges were moved closer to the table. The detonation table was placed in the center of a $30.5\text{-}\times30.5\text{-m}$ (approximately 930 m^2 , $100\times100 \text{ ft}$) tarp made of 18-ounce (509-g) flame resistant white vinyl. The tarp was used to facilitate recovery of residues.

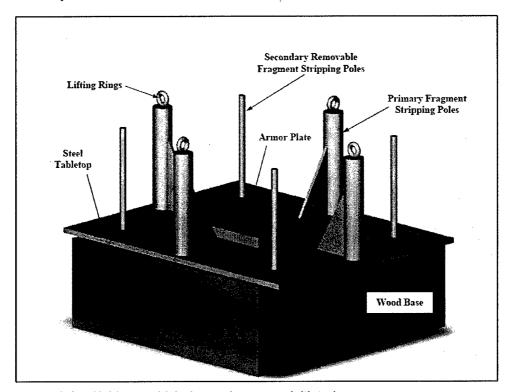


Figure 3-3. Table on which detonations were initiated.

Detonation properties

Blast pressure was measured by four PCB Piezotronics Free Field Blast Probe pressure gauges (PCB Piezotronics, Depew, NY) oriented in horizontal alignment 3 m from the center of the table and directly behind the protective columns. An additional gauge was placed 4.5 m from the table center on the side closest to the EOD tool. This gauge confirmed the asymmetric pressure data produced when the EOD tool was tested and provided data to allow the contribution of the EOD tool in each attempted low-order test to be separated from the ordnance response data.

Detonations were recorded by three high-speed cameras positioned at approximately 58, 78, and 240 m. Cameras recorded at approximately 10,000 frames per second and were protected in large portable steel bomb-proof shelters equipped with Lexan windows.

Specific wavelengths of light—600, 694, and 830 nm—were recorded with a three-channel radiometer developed by Applied Research Associates (ARA), Denver, CO. Ratios of low-order detonation bandwidths to those of high-order detonations were used to estimate the temperature of the blast. High-order detonations typically produced approximately 4000 K. The duration of the detonation was estimated by two techniques: the difference between pre- and post-detonation broadband light spectra collected with a total light radiometer, and the difference between pre- and post-detonation infrared spectra collected with an infrared unit.

The velocity of the penetrating jet was estimated from fiber optic cables attached to both the munition at the "aim" point and the low-order tool. Optical pulses created by breakage of the respective exposed glass fibers were converted to electrical signals by fiber optic receivers. Constant current, amplification, and data acquisition were assured by a signal conditioner. Detonation was initiated by a 30,000-V pulse from a fire-set device connected to the exploding bridge wire. An electronic sequencer was used to trigger all of the various instruments and initiated the fire set.

Detonation configurations

The test objective was to achieve at least four detonations at 75 percent energy yield and at least four at 50 percent energy yield for the 105-mm projectiles (Table 3-1). The 75 percent yield had been the most challenging energy yield to achieve in previous tests. Therefore, previous residue data from this energy level were limited. A decision tree was consulted to make systematic modifications to the test configuration as results of each configuration were received.

Typically, the first detonation for each type of munitions was a 25-g ball of C4 for verification of equipment performance. No residue data were collected from this detonation. The second detonation was a wax- or sand-filled inert munition. This detonation provided the pressure/energy yield contributed by the MK2 MOD 1 or the MCD without the explosive in the munition. The third detonation was initiated by 25 g of C4 packed into the fuze well of the munition. Although so-called "high-order" detonations are likely to generate a range of energy yields around 100 percent rather than a perfect maximum of 100 percent every time, this detonation was designed to represent the highest possible yield. Instrument responses for this detonation were taken to represent 100 percent pressure/energy yield calibration. Theoretically, this detonation consumed 100 percent of the explosive in the munition.

Table 3-1				
Test Configu	ırations*			
Shot number	Desired yield (%)	C4 (g)	Standoff (cm)	Attenuators
		60-mm [†]		
1 C4 alone**	100	NA	NA	NA
2 Inert (wax)	100	20	20.3	NA
3 100%	100	25 ^{††}	NA	NA
4	75	20	11.4	NA ·
5	75	15	15.2	NA
6	75	15	17.8	NA
7	75	15	15.2	NA
8	75	15	16.5	NA
		105-mm ^{***}		
10 C4	100	113.2	11.4	0
11	100	256	NA	NA
12	75	113.2	8.9	0
13	50	56.6	8.9	0
14	50	113.2	8.9	3
15	50	113.2	10.2	2
16	50	113.2	14	2
17	50	113.2	8.9	1
27	75	113.2	8.9	0
28	75	113.2	8.9	1
29	75	113.2	8.9	1
30	75	113.2	8.9	2
31	100	254	NA	NA
		155-mm		
18 inert (sand)	100	113.2	11.4	0
19	100	256	NA	NA
20	75	113.2	10.2	1
21	75	169.8	8.9	2
22	75	169.8	10.2	0
23	75	113.2	8.9	0
24	75	113.2	15.2	0
25	75	56.6	15.2	0
26	75	56.6	15.2	2

^{*} Angle of MCD was 90°.

All tests were conducted with unfuzed munitions to ensure the safety of EOD personnel. Previous experimentation with 155-mm artillery munitions had established that fuzed rounds detonated using an M42 shaped charge to penetrate through the side of the casing caused a full yield detonation (Blankenbiller and Lukens 1998).

[†] The MK2 MOD 1 tool was used to initiate the 60-mm mortars.

^{**} Shot consisted of a 226.8-g sphere of C4 detonated alone.

^{††} Since no MCD was used, the C4 was packed into the fuze well.

^{**} The MCD tool was used to initiate the 105-mm and 155-mm projectiles.

Residue Recovery

60-mm mortars (shots 1–8). For the 60-mm mortars, aluminum pans (66 \times 46 cm) were used to capture energetic material resulting from low-order detonations. Pans were placed in pairs at 305 (B), 610 (C), and 1524 (D) cm (10, 20, and 50 ft, respectively) from the table along four perpendicular transects (Figure 3-4). Four additional single pans (E) were place at 1143 cm (37.5 ft) between transects. Four pans (F) were also place on the corners of the tarp (2,155 cm, or 70.7 ft). Residues recovered from the surface of the table were designated A. Any chunk explosive retrieved from areas off the tarp were designated X collectively. After each detonation, residual material was removed from the pans and weighed. These values were used to estimate mass with distance. After removal of the pans, the tarp was swept in quadrants and the residue was weighed. These values were used to determine whether residue distribution was directionally related to placement of the tool. Residues from pans and the tarp were combined and sieved using brass standard soil sieves to the following sizes: >12.5, 4-12.5, 2-4, and 0.25-2.0 mm. The <0.25-mm size fraction was captured in the bottom pan of the sieve set. Each size fraction was weighed, and a small subsample, generally about 10 g, was reserved for chemical analyses.

Debris was manually removed from the >12.5-mm fraction, and the explosive residue remaining was weighed and assumed to be Composition B on the basis of visual inspection. Five-gram subsamples of the each of the remaining size fractions were extracted three times with 50-mL of acetone. Preliminary tests indicated that three extractions were sufficient to dissolve the explosive residue. Any unextracted residue, generally consisting of soil, gravel, metal fragments, grass, and bits of tarp, was weighed and considered nonexplosive. The extracts were combined, further diluted, and analyzed by Method 8330 for explosives and transformation products (EPA 1994).

105-mm (shots 10–17, 27–31) and 155-mm (shots 18–26) artillery projectiles. Since the direction in which residues were distributed proved unpredictable, the sampling approach was refocused on refining the estimation of distance from the detonation point with samples larger than those provided by the pans. Concentric circles were drawn on the surface of the tarp (Figure 3-5). The table (A), these donut-shaped areas (B–F), the remaining corners of the tarp (G), and the access tarp (H) were swept separately and the residues weighed. For these larger projectiles a concerted effort was made to retrieve visible residues landing beyond the tarp (X). All residues from a single detonation were combined and sieved, and a subsample of each size fraction (except chunks >12.5 mm, which were handled as previously described) was collected for extraction and chemical analysis by the methods described above.

Microscopic analysis of particles. Particles were collected on trays during detonations of five of the 60-mm mortars and three of the 105-mm artillery projectiles to obtain information on the number and appearance of high-explosive particles as a function of distance from detonation. Eight trays were located at 2-m intervals along one diagonal of the tarp starting 3 m from the detonation point. After the detonation, the material on each tray was weighed and sieved into <0.25-, 0.25- to 2.0-, and >2.00mm size fractions. The explosive particles

larger than 0.25 mm were separated from other debris under a light microscope. These Composition B particles were digitally photographed through the microscope; the pictures were loaded into a computer and digitally processed using a National Institutes of Health Image Program (a public domain program at http://rsb.info.nih.gov/nih-image) to obtain the number of particles and length of major and minor axes (Taylor et al. 2004). These axes measurements were used to calculate an average diameter of each particle.

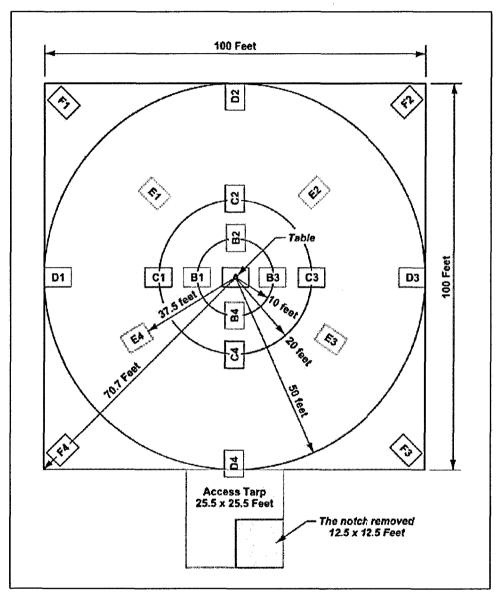


Figure 3-4. Schematic of table and pan locations on the tarp

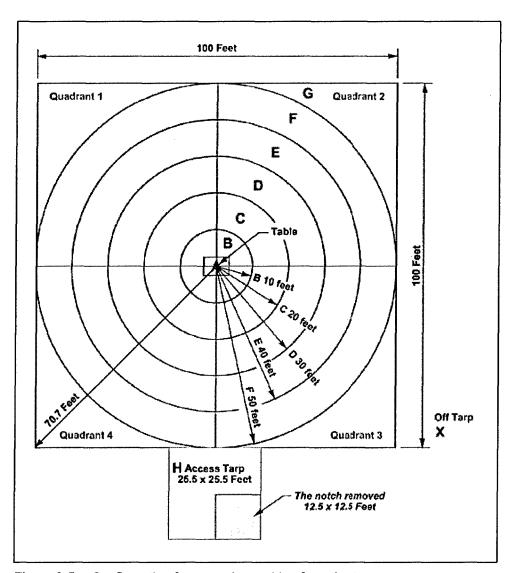


Figure 3-5. Configuration for sweeping residue from the tarp

Results

Energy Yields

The 60-mm mortars yielded either high or extremely low energy (Table 3-2). To achieve low-order detonations, a balance must be achieved between forces that sustain the detonation reactions and those that quench them. Use of the MK 2 MOD 1 shaped charge as a penetrator creates a vent hole in the casing of the mortar to aid in quenching a reaction that occurs in the warhead. The venting can allow for quick release of the confined pressure, which normally sustains or accelerates the reaction up to a transition into a detonation, or until all of the explosive is consumed. When the vent is so large as to allow pressure to dissipate too quickly, very low performance is observed, e.g., 2 percent energy yields (Shots 6 and 8). When the vent is insufficient, the pressure propagates until all, or nearly all, of the energetic material is consumed, e.g., >90 percent energy yields

(Shot 7). The small size of the mortar may permit the pressure to rise quickly in the limited volume and detonate all or most of the energetic material. Additional experimentation will be required to control the energy yield from these small munitions.

After the first set (Shots 13–17), more predictable results were achieved with the 105-mm projectiles (Shots 28–31) than with the 60-mm mortars (Table 3-3). The 105-mm projectiles have a thicker casing than the 60-mm mortars, and the MCD has a lower impact speed than the MK 2 MOD 1, which should reduce the amount and rate of pressure increase and result in greater control of energy yields. Fine adjustment in the use of the MCD, e.g., speed of the penetrator, quantity of C4, and addition of attenuators, provided greater flexibility in controlling variables important to detonation properties (Shots 17, 28–31, Table 3-3). Anticipating energy yields with 105-mm projectiles will be improved in future tests as a result of these tests.

The desired energy yields were not achieved with the 155-mm projectiles (Shots 19–26, Table 3-3). The assumption that targeting the thinnest area of the casing would result in the highest energy yields proved unreliable. Yields tended to increase when the impact point was moved from midway up the ordnance item to an area near the base where the casing was thickest. Controlling energy yields for these rounds pose a challenge for further testing.

Table 3-2
Mass (g) of Explosive Retrieved from Four Quadrants of the Tarp after Low-order
Detonations of 60-mm and 105-mm Rounds*

	Energy	Quadrant											
Shot number	yield (%) [†]	1		2		3		4	Total mass				
	60-mm**												
6	2.1	4.93		5.83		122.	70	4.93	138.39				
7	96	2.83		2.85		3.05		1.59	10.32				
8	2.4	7.46		198.2	9	4.97		7.81	218.5 [†]				
Mean		5.073		68.99)	43.5	7	4.78					
Standard Deviation		2.32		111.9	9	68.5	3	3.11					
			105-	-mm									
12	65	59.98	79.40)	38.5	6	36.	41	214.35				
13	10	75.33	414.8	37***	160.	80	65.	91	716.19				
14	22	52.23	70.89)	903.	10***	18.	68	1044.87				
15	14	56.34	80.48	3	144.	86	120).72	402.40 ^{†††}				
16	9	61.36	89.27	,	513.	90***	33.	04	697.97				
17	78	36.05	36.05 61.79		97.8	4	319	9.27	514.95				
Mean		56.88	132.7	'8	309.	72	99.	0050					
Standard Deviation		12.85	138.5	51	335.	20	113	3.85					

^{*} Data do not include residues from the access apron, large chunks remaining on the table, or residues recovered beyond the tarp; calibration shots (C4 alone, 100% energy yields, and inert shots) are also excluded from the table.

 † Values are average of peak pressure, incident impulse, and incident impulse at 500 μ s.

** Data from shots 4 and 5 were lost.

*** Values are inflated by the presence of large chunks of explosive residue.

^{††} Although this value exceeds the quantity of explosive typically placed into mortars, 190–200 g, the value is within experimental error.

ttt A large portion of the round (648 g) remaining on the table was not included in this weight.

Relationship between energy yield and mass recovered

The quantity of Composition B in 60-mm mortars varies from 190 to 200 g (approximately 0.42 lb). As anticipated, the mass of explosive for the two 2 percent energy yield detonations (Shots 6 and 8) was larger than for the detonation exhibiting 96 percent energy yield (Shot 7, Tables 3-2 and 3-3); however, because of the small sample size, no significant correlations were found between energy yield and total mass recovered (Pearson Product Moment Correlation analysis and Spearman Correlation analysis on ranks). Energy yields for the 105-mm projectiles were negatively correlated with residues of Composition B recovered according to the Pearson Product Moment Correlation Analysis, correlation coefficient = -0.81, P = 0.004. Spearman Rank Order Correlation Analysis did not show this relationship (correlation coefficient = -0.576, P = 0.07). A negative correlation of mass and energy yield was demonstrated for the 155-mm projectiles (Pearson Product Moment correlation coefficient = -0.785, P = 0.0365; Spearman Rank Order Correlation Analysis, correlation coefficient = -0.881, P = 0.000). When mass expected on the basis of energy yields for all rounds is regressed against actual recovery, the slope of the regression is 2.65 (r² = 0.63, Figure 3-6). Therefore, energy yields tend to overestimate mass recovered. In the 105-mm munitions the average difference between mass expected on the basis of energy yield (650 g of the initial mass of 2,408 g) and mass recovered (174 g) was about 73 percent. For the 155-mm munitions (initial mass of 6,622 g) the average difference was about 79 percent. Some of the difference between mass based on energy yields and mass recovered from the tarp may be attributable to unrecovered mass falling beyond the tarp. Differences attributable to the measurement techniques (pressure sensors for energy yields and mass recovered by sweeping the tarp) and those attributable to loss beyond the tarp cannot be resolved.

Relationship between mass recovered and areal distribution

Because of the high variability occasioned by the presence of chunk material, and the limited sample size, no significant differences among the four quadrants were observed for the 60-mm mortars (P = 0.585) nor for the 105-mm projectiles (shots 12–17, P = 0.139, Table 3-2). Therefore, directionality of residue deposition relative to the position of the MCD remains uncertain. For the remaining 105-mm detonations (shots 27–30) and for the 155-mm detonations (shots 19–26), data acquisition by quadrant was abandoned in favor of data by distance in concentric circles around the detonation center (Figure 3-5). Pans captured a relatively small fraction of the residues and were not always located optimally for capturing a representative mass of the residue as a function of distance from the detonation. Therefore, pans were also abandoned in favor of sweeping the tarp.

Recovered mass for both the 105- and 155-mm projectiles increased with distance from the detonation center (Figures 3-7 and 3-8). This result suggests that significant mass may have fallen beyond the tarp. Differences between mass expected on the basis of measure energy yield and total mass recovered from the tarp (see "Relationship between energy yield and mass recovered" above) also suggest a loss of mass beyond the tarp for these rounds. The mass from 155-mm projectiles at higher energies (>18 percent) declined, or at least leveled off,

toward the edge of the tarp (beyond 40 ft). Although visual observation of residues on the tarp indicated a lack of uniform symmetry in the distribution of residuals around the center of the detonation (the table), mass with distance results suggest that mass peaks at some distance from the detonation center and then decreases with additional distance. The peak distance may be related to the energy yield. However, when the mass is averaged for all energy yields, the mass increases with distance from the detonations for both the 105- and 155-mm rounds (Figure 3-9).

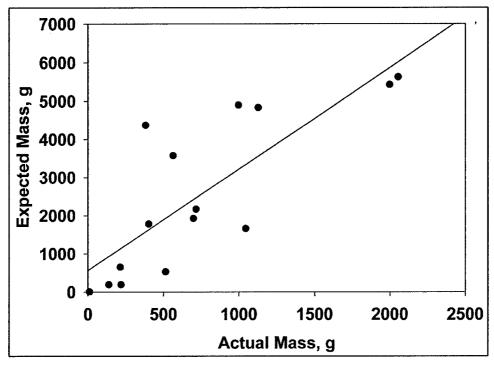


Figure 3-6. Mass of explosive residue based on the energy yield measured by the pressure gauges (expected mass) versus the mass actually recovered from the tarp (actual mass). Slope = 2.65, y-axis intercept = 563, and $R^2 = 0.63$.

When an ANOVA was performed on the data for mass by distance from the detonation of 105-mm projectiles (Shots 27–30), differences were detected (P = 0.048); however, a test for normality failed. Results of the Holm-Sidak Method of Multiple Comparisons (an all pair-wise multiple comparison procedure) indicated significantly greater mass in the two outer rings (between 30 and 50 ft) than on the table or within 10 ft of the detonation center (Table 3-4, Figure 3-7). Similar results were observed in the 155-mm data, although results of an ANOVA indicated no significant differences (P = 0.341) because of the high variability (Table 3-4, Figure 3-8). The elevated values for Shots 21 and 22 represent a single large portion of the round that remained on the table after detonation.

Table 3-4 Mass (g) of Explosive Residues Retrieved from the Seven Rings of the Tarp after Loworder Detonations of 105- and 155-mm Mortars

	Energy yield		Distance from Detonation (ft)									
Shot number	(%)*	Table	10	20	30	40	50	Corners	Total			
105-mm												
27	78	0.22	4.17	5.14	12.25	25.85	25.85	59.70	133.18			
28	73	0.53	5.52	8.59	15.38	31.050	56.13	43.74	160.94			
29	67	0.78	8.13	9.48	12.66	62.17	56.13	36.9	186.25			
30	52	1.79	15.89	37.70	72.71	90.030	62.46	40.54	321.12			
31	100	0.080	0.36	0.69	1.95	4.92	7.52	10.88	26.40			
Mean	74	0.68	6.81	12.32	22.98	42.800	41.62	38.350	165.58			
Standard Deviation	18	0.68	5.80	14.025	28.26	33.41	23.81	17.65	106.14			
				155-mm ¹								
19	100	0.06	0.12	0.27	3.95	3.71	3.28	1.92	13.32			
20	15	37.27	50.010	84.18	321.070	552.94	692.53	315.47	2053.47			
22	18	851.95	57.58	126.33	179.54	219.65	339.16	203.28	1997.49			
23	27	2.080	2.70	73.52	455.60	297.18	178.51	118.25	1127.83			
24	26	14.85	69.68	146.57	209.19	235.29	184.40	137.44	997.43			
25	34	1.050	17.060	29.00	56.32	102.17	76.72	98.72	381.040			
26	46	0.91	17.67	21.76	51.89	109.52	109.52	252.91	564.18			
Mean	38	129.74	30.69	68.80	182.51	217.21	226.30	161.14	1019.25			
Standard Deviation	29.2	318.75	27.96	54.94	162.98	177.88	230.90	104.61	781.58			
												

Based on average of peak pressure, incident impulse, and incident impulse at 500 μs . One sample from shot 21 was lost; therefore, remaining data from that shot are excluded.

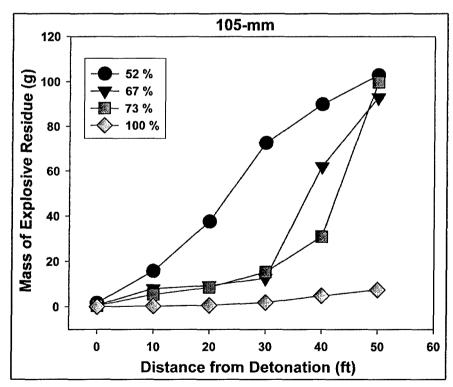


Figure 3-7. Mass recovered with distance for each energy level achieved with the 105-mm artillery projectiles

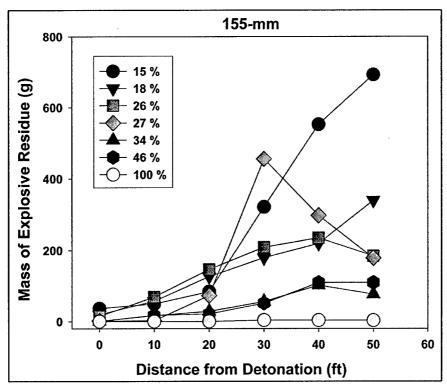


Figure 3-8. Mass recovered with distance for each energy level achieved with the 155-mm artillery projectiles. The graph does not reflect the large chunk at 0 distance (on the table) and 18 percent energy yield

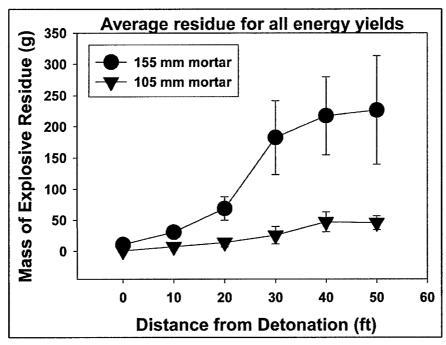


Figure 3-9. Average residue mass recovered over all energy yields with distance from detonation center

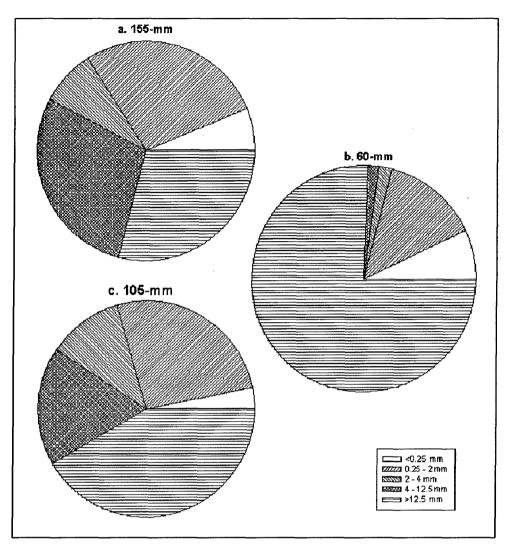


Figure 3-10. Mass recovered by particle size distribution. a. 155-mm artillery projectile particle size values are means from eight shots having a mean energy yield of 35.6 ± 27.9 percent. b. 60-mm mortar particle size values are means from three shots having energy yields of 2.1, 96, and 2.4 percent. c. 105-mm artillery projectile particle size values are means from 10 shots having a mean energy yield of 46 ± 29.3 percent (including a 100 percent energy yield)

Particle size distribution

Sieve analyses. The mass in the >12.5-mm size fraction of residues from 60-mm mortars at 2 percent energy yields was substantial relative to the mass of other size fractions (Shots 6 and 8, Table 3-3, Figure 3-11). At the higher energy yield (Shot 7) all of the residue was in the smaller size fractions (<4 mm, Table 3-3). For the 105-mm projectiles the mass by size fraction data were not normally distributed; however, results of an ANOVA indicated that differences among means were greater than would be expected by chance (P = 0.031) (Table 3-3). When the Holm–Sidak Procedure was applied, the mass of the >12.5-mm size fraction was significantly greater than the mass of the 2-4 and the

<0.25-mm size fractions. This is likely a result of the chunk material in the larger size fraction and heterogeneous distribution in other particle size fractions. For the 155-mm projectiles, the particle size distribution data failed the test for normality (P = 0.003); the variability in the data was too high to detect any significant differences in mass by particle size distribution. However, large chunks not traveling very far from the detonation center are reflected in the data for the >12.5- and 4- to 12.5-mm fractions (Table 3-3).

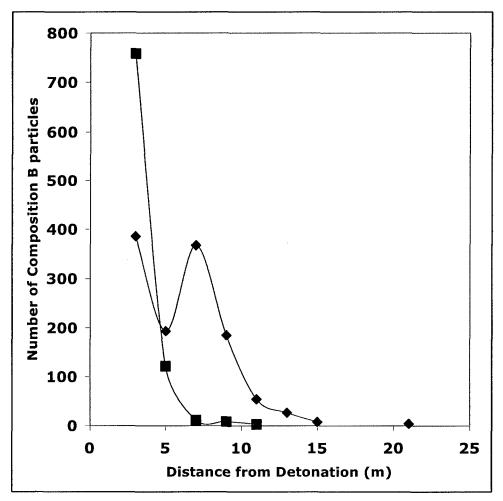


Figure 3-11. Average number of explosive particles in the >0.25-mm size fraction as a function of distance from the detonation. Data include 60-(diamonds) and 105-mm (squares) detonations.

Appearance and number of HE particles on pans. Microscopic observations show that the residues contained rounded and lumpy particles of Composition B, melted metal spheres, aluminum, other metal fragments, large pieces of wood from the tool stand, and soil (Figure 3-11). Close to the detonation the explosive particles from the sampled rounds were similar in size and range between 0.40 and 0.80 mm. With distance from the detonation the particle size increased and then decreased, with the peak in particle size occurring at \sim 7 m (23 ft) and 13 m (43 ft), respectively (Figure 3-12). The average number of particles in the >0.25-mm fraction also decreased with time except for a spike at about 7 m for the 60-mm mortars (Figure 3-12).

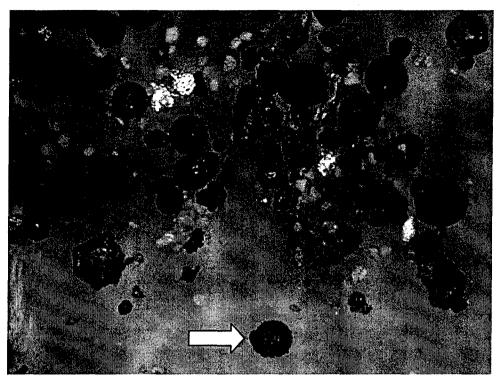


Figure 3-12. Photomicrograph of particulate residue from low-order detonation.

The round and sub-round particles are Composition B (for example, see arrow)

Chemical composition of residues

The ratio of TNT to RDX in residues from the 60-mm mortars was variable (Table 3-5). In the two low-energy detonations, Shots 6 and 8, the ratios were 1 to 0.88 and 1 to 1.49, respectively. In the higher-energy shot, Shot 7, the ratio was 1 to 2.05. The ratio in undetonated Composition B is typically 1 to 1.5 Small amounts of HMX (an average of 3.52 ± 2.97 percent of the total mass) and TNB (an average of 0.09 ± 0.07 percent of the total mass) were also detected. These probably occurred as impurities in the Composition B. The TNB, however, may have formed after detonation because of exposure of residues to sunlight.

The ratio of TNT to RDX in residues from the 105-mm projectiles was relatively consistent and very near the assumed ratio before detonation (1 to 1.5). The mean ratio of TNT to RDX was 1 to 1.47 ± 0.15 . Other detections were HMX and TNB, with means of 3.58 ± 1.11 percent and 0.02 ± 0.03 percent of the total mass, respectively. DNB was detected in four of the detonation, but quantities were less than 0.01 g (<0.001 percent).

			Size (mm)								
Shot number	Energy yield (%) [†]	>12.5	4–12.5	2–4	0.25-2	<0.25	Total				
	10.70	60-mm*	*								
6	2.1	93.6 ^{††}	2.9***	3.3***	24.4	2.8	136.8				
7	96	0	0	0.5***	7.1	2.7	10.3				
8	2.4	183.0 ^{††}	2.7	3.1	19.9	9.8	218.5 ^{†††}				
Mean	33.4	92.2	1.9	2.3	17.1	8.5	121.9				
Standard Deviation	54.1	91.5	1.6	1.6	9.0	5.2	104.9				
		105-mm	n								
12	65	0.2	3.7	27.5	169.2	13.8	214.4				
13	10	274.1	160.2	143.4	130.1	37.3	745.2				
14	22	671.8 ^{††}	131.9	73.5	150.0	17.9	1045.08				
15	14	648.0 ^{††}	79.2	101.0	208.4	14.6	1051.0				
16	9	498.7 ^{††}	220.5	85.8	130.5	35.2	970.2				
17	78	19.9	258.9	45.0	199.4	11.6	534.9				
27	76	0	4.0	22.9	124.7	9.4	161.0				
28	73	0	23.7	35.3	120.6	6.7	186.3				
29	67	21.9	55.8	56.1	191.3	18.0	343.0				
30	52	0	3.4	4.8	9.5	5.8	23.4				
Mean	46.6	213.5	94.1	59.5	143.4	17.03	527.4				
Standard Deviation	29.3	286.8	94.4	41.9	57.3	11.0	397.5				
		155-mm	n								
19	100	0	0	1.8	7.1	4.4	13.3				
20	15	738.0	1310.9	149.9	499.5	16.9	2715.2				
21	19	1264.0 ^{††}	1138.6	278.8	ND***	54.3	2735.7				
22	18	1022.0 ^{††}	297.4	141.4	591.8	83.7	2136.4				
23	27	62.9	127.4	126.9	422.7	437.2	1177.2				
24	26	99.5	151.0	175.6	584.9	64.7	1075.7				
25	34	35.4	78.9	37.5	291.9	21.6	465.2				
26	46	55.6	147.7	27.3	359.6	20.7	611.0				
Mean	35.6	409.7	406.5	117.4	393.9	87.93	1366.2				
Standard Deviation	27.9	515.8	513.9	91.8	203.6	143.2	1043.4				

^{*} Data presented are the sum of all explosives in each fraction from the table, the tarp, the access apron and off the tarp.

The 155-mm artillery projectiles were TNT-filled. Therefore, residues were predominantly TNT. However, an average of 0.05 percent of the total residue recovered was RDX; HMX was detected in the residue from one detonation (8 percent); and TNB was detected in residues from six of the eight detonations (averaging 0.01 ± 0.008 percent of total mass). These compounds may have been present in the TNT as impurities or may have been present on the tarp from prior detonations of Composition B rounds. The single high-HMX detection is difficult to understand and may represent an anomaly in that specific round. The TNB may have formed by photolysis on the surface of the TNT particles between the time the detonations were completed and the samples were collected. Red coloration of the tarp, and occasionally red coloration of residue particles, was observed.

[†] Values are average of peak pressure, incident impulse, and incident impulse at 500 µsec.

^{**} Data from shots 4 and 5 were lost.

^{††} Represents a single chunk of explosives.

^{***} No visible explosive in residue; however, HPLC analysis resulted in detection of explosives.

this value exceeds the quantity of explosive in the mortar, 199 g, the value is within experimental error.

Table 3-5 Chemical Composition of Residues (g)														
Shot number	Energy yield (%)	Ratio of TNT:RDX (1:x)	TNT	RDX	нмх	TNB								
	60-mm													
6	2.1	0.88	71.40	63.02	3.92	0.05								
7	96	2.05	3.15	6.45	0.70	0.18								
8	2.4	1.49	86.72	129.61	2.09	0.11								
105-mm														
12	65	1.68	75.50	127.06	11.58	0.20								
13	10	1.49	290.15	432.34	22.16	0.28								
14	22	1.49	428.99	640.14	23.52	0.29								
15	14	1.46	419.72	614.14	26.10	0.16								
16	9	1.65	359.11	590.91	21.61	0.073								
17	78	1.51	207.30	312.87	14.68	0.042								
27	76	1.27	56.27	71.24	5.66	<d.l.< td=""></d.l.<>								
28	73	1.41	63.66	89.71	7.55	0.024								
29	67	1.49	71.47	106.83	7.96	<d.l.< td=""></d.l.<>								
30	52	1.51	131.26	197.78	13.88	<d.l.< td=""></d.l.<>								
31	100	1.16	11.71	13.58	1.11	<d.l.< td=""></d.l.<>								
		155-mm	***************************************	***************************************										
19	100	2.28*	3.72	8.47	1.12	<d.l.< td=""></d.l.<>								
20	15	1.7 e-3	2710.43	4.72	<d.l.< td=""><td>0.32</td></d.l.<>	0.32								
21	19	7.8 e-5	2735.47	0.21	<d.l.< td=""><td><d.l.< td=""></d.l.<></td></d.l.<>	<d.l.< td=""></d.l.<>								
22	18	1.8 e-4	2135.87	0.382	<d.l.< td=""><td>0.44</td></d.l.<>	0.44								
23	27	4.8 e-4	1176.48	0.57	<d.l.< td=""><td>0.14</td></d.l.<>	0.14								
24	26	3.5 e-4	1075.16	0.38	<d.l.< td=""><td><d.l.< td=""></d.l.<></td></d.l.<>	<d.l.< td=""></d.l.<>								
25	34	4.1 e-4	416.18	0.17	<d.l.< td=""><td>0.053</td></d.l.<>	0.053								
26	46	4.5 e-4	619.51	0.28	<d.l.< td=""><td>0.014</td></d.l.<>	0.014								

^{*} The detection of a relative high mass of RDX in these first two shots suggests the presence of carry-over residue from previous shots. The 155-mm projectiles contained TNT only.

Conclusions

Achieving predictable energy yields was challenging, especially for the 60-mm mortars. The small size of the 60-mm data set further limited the determination of relationships between energy and residues. However, energy yield was inversely related to residual mass in detonations of 105- and 155-mm projectiles. Therefore, the measured over-pressure is related to the amount of explosive residue likely to be generated by low-order detonations of these munitions. Directionality in the distribution of residues was inconsistent. However, the mass from 105-mm projectiles was significantly greater at 50 and 70 ft than on the table and at 10 ft. These results did not hold for the residues of 155-mm projectiles, for which no significant differences in distribution by distance were measured. However, the 155-mm data do reflect the presence of large chucks of explosive that did not travel far from the detonation point, e.g., remnants of the base of the item remained on the table or on the ground near the table.

Although the >12.5-mm size fraction contained the greatest mass and the < 0.25-mm fraction contained the smallest mass for each munition, the relationship between particle size and mass was not linear. The size fraction of 2-4 mm was inexplicably poorly represented. The preponderance of large chunks versus fines suggests relatively slow release potential of the explosives from the solid to the solution phase over time. Most of the residual mass from the 60-mm mortars was deposited within 7 m of the detonation. This result suggests that most of the residue from this round was captured by the tarp.

The ratio of TNT to RDX in pre-detonation Composition B was generally reflected in the post-detonation composition. The small amounts of HMX residues were likely present as impurities in the pre-detonation Composition B. Detectable levels of TNB were either present pre-detonation as impurities or may have formed post-detonation because of exposure of the residue to sunlight.

Results indicate an inverse relationship between the over-pressure of the blast and the mass of explosives residual. Furthermore, low-order detonations contribute predominantly large particles of solid Composition B to the source term for ranges. Therefore, the ratio of TNT to RDX in these particles is conserved. Transport will depend heavily on dissolution rates of TNT and RDX from the solid-phase compositions and subsequent interactions between dissolved constituents and the soil.

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4 Environmental Conditions of Surface Soils, CFB Gagetown Training Area: Delineation of the Presence of Munitions-Related Residues (Phase III)

This chapter is an abstract of the following published technical report:

Thiboutot, S., Ampleman, G., Marois, A., Gagnon, A., Bouchard, M., Hewitt, A., Jenkins, T., Walsh, M., Bjella, K., Ramsey, C., and Ranney, T. A. (2004). "Environmental conditions of surface soils, CFB Gagetown Training Area: Delineation of the presence of munitions related residues (Phase III, Final Report)," DRDC-Valcartier TR-2004-205, Defence Research and Development Canada-Valcartier, Quebec.

Introduction

Troop readiness requires intensive training in Canada. Moreover, many other countries use Canadian training ranges under international agreements. Testing and training ranges are key elements in maintaining the capability, readiness, and interoperability of the Armed Forces. The potential for environmental impacts of live-fire training mandates that our organizations demonstrate responsible management of these facilities in order to continue testing and training. The most extensive study achieved up to now was conducted at Dundurn open detonation range, where the impact of the open detonation of Canadian obsolete munitions was extensively studied (Ampleman et al. 1998). The first training range visited was the CFB Shilo training area, where research demonstrated the environmental impacts of many types of live-fire training (Thiboutot et al. 2001, Ampleman et al. 2003. Antitank firing ranges across Canada were also the topic of other studies (Thiboutot et al. 1998b, Arel et al. 2002, Marois et al. 2004). Moreover, many papers were written in recent years concerning the fate and analysis of explosives at various types of sites (Jenkins and Walsh 1987, Checkai et al. 1993, EPA 1993, Jenkins et al. 1997a, 1997b, 1998, 1999, 2001, 2003, Thiboutot et al. 1997, 1998, 2000, 2002, 2003a, 2003b, Walsh and Ranney 1998, 1999,

Ampleman et al. 2000, Miyares and Jenkins 2000, Walsh et al. 2002, 2004, Pennington et al. 2002, 2003, Hewitt and Walsh 2003, Stamfli et al. 2003, Hewitt et al. 2004).

Military training exercises have been conducted on CFB Gagetown since 1954. Currently, this base serves as one of the major training facilities for the Canadian Forces and is also used by troops from the United States, United Kingdom, and Australia. It is the main training area for eastern Canada where most of the long-range, high-caliber, live firing is conducted. The base is located 20 km southeast of Fredericton, New Brunswick, and covers an area of about 1100 km² (Figure 4-1).

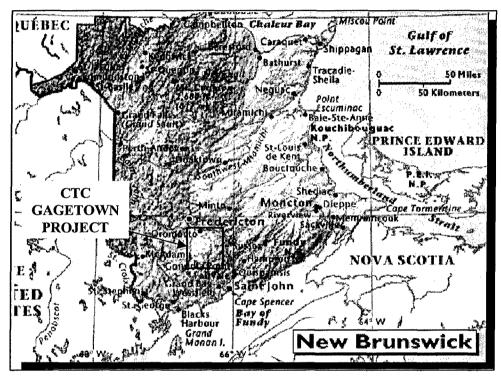


Figure 4-1. Gagetown Area Map

Approximately half of this territory serves as Static Range Impact Areas (SRIA) for infantry, artillery, air defense, engineer, and armored vehicle live-fire training, while the southern portion of the area is used as a general maneuver area. Recently, awareness has increased that the energetic residues and heavy metals associated with munitions can be released to the environment during training activities and over time potentially contaminate the underlying groundwater. For instance, munitions training and testing exercises were suspended at the Massachusetts Military Reservation following the discovery of low concentrations of RDX in the groundwater beneath the main training area (EPA Order Number 2). On military training ranges, munitions-related pollutants can be released to the environment from breaches in the casings of unexploded ordnance (UXO) or partially exploded ordnance; from poor disposal practices, such as unconfined burn operations; from blow-in-place operations; and from live-fire operations. The Strategic Environmental Research and Development Program (SERDP) funded several studies directed at assessing thef source strengths and

pathways of munitions residues on military training facilities. Moreover, Director Land Environment (DLE) tasked DRDC-Valcartier to initiate a research program for the environmental characterization of their main training areas. The work carried out at CFB Gagetown was co-sponsored by both programs.

This chapter presents the results of the third characterization (Phase III) carried out at CFB Gagetown training area. The first phase was conducted in the fall of 2001 and was dedicated to the drilling of wells on the northern half of the base to collect groundwater samples and to perform the hydrogeological characterization of the site (Thiboutot et al. 2003a). Phase II consisted of both surface and subsurface characterization, where more wells were drilled and sampled in the southern half of the base and surface soils and biomass samples were collected (Thiboutot et al. 2003b). The results of Phase II indicated a need to resample the five following areas: background, antitank range, grenade ranges, propellant burn pads, and small arms ranges. The objectives of the sampling effort in 2003 were to define the spatial distribution and fate of metals and energetic residues. Fieldwork was conducted in the fall of 2003, and data treatment was done in the winter and spring of 2004. A more extensive report on the same topic was published as a DRDC report (Thiboutot et al. 2004).

Experimental

Field Investigation

Fieldwork was conducted between October 20 and October 25, 2003, at CFB Gagetown, in the training area and around base limits for background sample collection. Surface sampling was concentrated in the live-fire impact areas located in the northern portion of the base. Sampling strategies were designed on site, depending on the landscape, visual observations of the area, information gathered from the Explosive Ordnance Disposal (EOD) unit personnel, and experience gained in the previous Gagetown study (Thiboutot et al. 2003b).

Chemical Parameters and Analytical Methods

Energetic materials were analyzed by using high-pressure liquid chromatography (HPLC) and gas chromatography (GC-ECD) following EPA Methods 8330 and 8095 (EPA 1994, 2000). Metals were analyzed by inductively coupled plasma mass spectrometry (ICP/MS) by RPC Laboratory (Fredericton, NB, Canada). All parameters available by this method were included. For some specific samples, soil leachate tests were done (TCLP procedure) (EPA 1992, 1996).

Sample Handling and Treatment

The samples collected in this study were of the top 2 cm of the surface soil. In addition, sediment, surface water, and three soil profile samples at multiple discrete intervals were collected. Composite samples were stored in polyethylene bags, while the sediment, soil profile, and water samples were stored in amber glass bottles with Teflon-lined caps. The water samples were stored in 500-mL

amber bottles, and the discrete soil and sediment samples were stored in 120-mL bottles. The samples were refrigerated with ice and sent to CRREL for processing and analysis. For metals analysis, samples were either sent directly to RPC laboratory or sent back from CRREL to RPC after homogenization of the main bulk samples. Results for metals were analyzed by Dr. Thiboutot at DRDC Valcartier.

At CRREL all of the soil and sediment samples were air-dried, then passed through a 2-mm sieve. Following sieving, subsamples were removed from all of the samples for the metal analysis with the exception of the background and burn pad samples. Both the background and burn pad samples were equally divided in the field, and sample splits were shipped to both CRREL and a contract laboratory. All of the samples were ground in a ring mill (Labtech EssaLM2) for 60 s, then a 10-g subsample was removed by randomly obtaining 30 or more increments and transferring them into 40-mL glass vials with Teflon-lined septum caps. Acetonitrile was added directly to the soil and sediment samples (120-mL glass bottles). The volume of solvent was twice the weight of the air-dried (< 2 mm) soil. After the addition of acetonitrile, the sample jars were shaken on a platform shaker at 200 rpm for 18 hours. To assess the sample processing protocol (grinding and subsampling), triplicate subsamples were removed for extraction and analysis for one out of every ten composite samples. After the addition of 20 mL of acetonitrile to each vial, the subsamples were extracted in a temperature-controlled sonic bath for 18 hours. Following extraction by either shaker table or sonic bath, an aliquot of the solvent extract was filtered through a 0.45-µm, 25-mm Millex FH filter. The water samples were first pre-concentrated through a solid-phase extraction (SPE) cartridge (Jenkins et al. 1997b). This technique retains the energetic residues on a Porapak RDX cartridge (Sep-Pak, 6-cm³, 500 mg), which was subsequently eluted with 5.00 mL of acetonitrile.

Sample analysis

For energetic materials, samples were analyzed by either GC-ECD (EPA 2000) or HPLC (EPA 1994), or both. The GC was an HP6890 equipped with a micro-cell Ni63 ECD, and the analysis protocol followed the EPA SW-846 Method 8095 guidelines (Walsh and Ranney 1998, 1999). Primary and secondary GC-ECD analyses were performed using a 7-m × 0.53-mm ID fused silica column, with a 0.5-μm coating of 5 percent-(phenyl)-methylsiloxane (RTX-5MS from Restek, Bellefonte, PA) and a 6-m × 0.53-mm ID fused silica column with a 1.0-µm coating of a proprietary phase (RDX-TNT-2 also from Restek), respectively. Reverse-phase (RP) HPLC analyses were performed on a modular system (Thermo Separation Products Inc., San Jose, CA) consisting of a P1000 isocratic pump, a UV2000 dual wavelength absorbance detector set at 210 and 254 nm, and an AS3000 auto sampler. Analyte separations were performed using the 15-cm × 3.9-mm (4-mm) NovaPack C-8 column (Waters Chromatography Division, Milford, MA) eluted with 15:85 isopropanol/water (v/v) at 1.4 mL/min. Samples with energetic residue concentrations greater than 200 µg/L were analyzed by RP-HPLC.

Metals were analyzed by RPC Laboratory by ICP/MS and total metal concentrations were obtained by using EPA Method 3050 (EPA 1996) involving a nitric acid/hydrogen peroxide digestion. Leachate testing used EPA Method

1311, which entails buffered acetic acid leaching at a 20:1 liquid to solid ratio (EPA 1992).

Range Description and Sampling Strategy

The surface sampling team collected 189 soil samples in the following areas: background samples outside the live-fire training area (14 samples), New Castle Rifle and Hand Grenade Ranges (7 and 18 samples, respectively), Wellington Antitank Range (115 samples), Vimy Small Arms Range (11 samples), propellants burn pads/locations (10 samples), and sets of samples before and after a 500-lb bomb and two heat rounds were blown in place (14 samples). In general, the main goal was to delineate more precisely the presence of munitions-related contaminants in the antitank and small arms ranges, to validate the presence or absence of TNT in background samples, and to evaluate the evolution with time of the contaminant concentrations in the grenade ranges. Seven water samples were also collected in ponds and craters in the antitank range. Many sampling patterns were used in the present study, based on our combined previous experiences, visual inspection, the presence or absence of targets, and the general settings of the ranges. Mostly surface soils (from 0 to 2 cm deep) were collected; however, some core samples were collected in specific areas of interest. The cores were collected with a manual corer designed by the CRREL team (Thiboutot et al. 2004). The surface sampling design used most frequently for this investigation involved collecting multiple increments within a designate area, while systematically moving from one end to the other. Along with this sampling protocol, samples were collected along linear transects to replicate the protocol used in 2002. Pits were also dug to allow subsurface sampling in the antitank range, both in the impact area and at the firing position (FP).

Background samples

In the 2002 study, TNT was detected in most of the sixteen background samples that were collected outside of the training area. It was imperative to resample the same locations in 2003 to verify if TNT cross-contamination was generated either in transport or during laboratory treatment. In 2003, fourteen samples were collected, including two field duplicates. During this investigation, all of these samples were kept in a separate cooler and never exposed to the other samples in order to avoid any risk of cross-contamination. The sampling locations were chosen as near as possible to the sampling location from last year's study.

Wellington Antitank Range

The Wellington Antitank Range (WAT) was covered with shrapnel and propellant residues. The range is located north of the Argus and Greenfield Impact Area and is approximately 5 km². Six tanks on the range at various distances from the firing position serve as targets for training with 66-mm M72 LAW M72E5 rockets and 84-mm rounds. Soil, sediment, and water samples were collected. Samples were collected in the target zone (impact zone), in front of and behind the firing position, and within an ordnance disposal bunker before and

immediately following the blow-in-place of two UXOs. Targets one to five were, respectively, the nearest and the farthest from the firing position, while target six was located on the other side of a small road within the range. Areas in front of and behind the targets had been strafed. Depressions in these strafed areas were filled with water, creating small pools where sediment and water samples were collected.

New Castle Hand Grenade Range

This is a relatively new range that has been in use for two years. Range control personnel were able to provide us with the exact number of hand grenades used (2459) since the range opened by consulting their logbook. The impact area in front of the cement throwing bunkers was 55 m wide and was covered with medium-grit sand and pebbles. Surface composite samples (0–2 cm) were collected along linear transects and in designated areas that were parallel to the throwing bunker, using similar sampling strategy as used at the firing point. Single and duplicate 30-increment composite samples were collected on the right and left sides of the impact range. These 11 samples were collected to assess whether munitions-related residues could be found on each side of the range and at a farther distance behind the range.

40-mm New Castle Rifle Grenade Range

This training range for 40-mm rifle grenades also had only been operational for a little more than one year. Range control was able to provide us with the number of rifle grenades fired on the range since its opening (1206). In a zone 100–130 m downrange from the firing line, three 30-increment composite samples were collected, one for each third of the range going left to right. This same sampling pattern was repeated in a zone 170–200 m downrange behind a second pair of targets. One duplicate composite sample was collected on this impact range, behind the left 160-m target.

Blow-in-Place Location of 500-lb Bomb

Surface samples and a single water sample were collected on Hersey Impact Range where an Mk82 500-lb bomb (82 kg tritonal, 80 percent TNT, 20 percent aluminum) had landed and was blown-in-place. Prior to detonation with the use of three blocks of C4, surface soil samples were collected around the bomb using a stainless steel coring tool in a circle approximately 5 m in diameter. Cores were split into two sections (0–3 cm top, 3–6 cm bottom). Ten-increment composites were collected around the UXO before and after the detonation. The detonation formed a crater approximately 2.5 m deep and 8 m in diameter. The soil from the crater covered most of the surface that had been sampled prior to detonation. Triplicate composite surface (0–2 cm) soil samples comprising more than 63 increments were collected within the crater by systematically taking increments at 1-m² intervals. Likewise, triplicate, randomly located 55-increment composite samples were collected while systemically moving around the crater covering an area 0–10 m from the rim. Between 10 and 20 m from the rim, duplicate 25-

increment composite samples were collected using this same strategy; however, the coring tool was used to obtain the top 2 cm of the crater.

Burning Pads

A recent decision was made at the Gagetown training area to bring excess artillery propellant to two centralized locations for burning, as opposed to burning in the field wherever the artillery guns happened to be firing. Therefore, two concrete burn pads approximately 2 m × 2 m × 20 cm thick were installed at each burn location in order to prevent the residues from contaminating the soil. The surroundings of the eight burning pads were sampled to verify the localized impact of this activity in both 2002 (only two locations, four samples) and in 2003 (four locations, eight samples). At all locations, despite the presence of the concrete pad, large amounts of propellant had obviously been burned on the adjacent ground. The soil in rain run-off channels and in burn marks immediately beside the pads was sampled. The samples were composites of at least 25 increments. In general, the sampling area was between 0 and 1 m outside of the concrete pad limit.

Vimy Small Arms Range

In 2002 three small arms ranges were sampled to verify their potential contamination by heavy metals. In 2003 the Vimy Small Arms Range was resampled to verify the evolution of the contamination with time, to include the firing lines in the sampling study, and to run leachate tests (TCLP) on the soil samples to verify the bioavailability of the metal analytes. Eleven composite soil samples were collected in front of three groups of targets. Composite samples (25 discrete each) were collected at 100-, 200-, and 300-m firing lines.

Results and Discussion

Summary of 2002 Results (Phase II)

General conclusions from the Phase II study are that the Anti-Armour Range and Wellington Antitank Rocket Range are impacted by various heavy metals and explosive residues, both at levels of concern. The most contaminated areas were found near targets and to the front and rear of firing positions. Artillery ranges were mainly impacted by Cd, Cr, Zn, and Pb but in localized target areas. Metals were also detected in high concentrations at target areas or in craters in artillery impact areas. The contaminants of concern in the artillery ranges are Cd, Cu, and Zn. Argus Range presented the highest concentrations of metals, followed by Lawfield, Hersey, and Greenfield Impact Areas. Explosive residues were detected at lower concentrations on artillery ranges than on the Anti-Armour Range and Wellington Antitank Rocket Range. Grenade ranges also presented mixed contamination by both metals and energetic materials, with the oldest range being the most highly impacted area. The burning area had high concentrations of Pb, Sr, and 2,4-DNT. Finally, small arms ranges (SAR) were heavily impacted by Pb and other heavy metals. In general, trends that were

identified for soil accumulation were correlated with vegetation results for the 2002 study. Results of the 2002 study led to the following objectives for 2003: to further develop our understanding of the spatial distribution of metals and explosives on five live-fire ranges, to assess vertical migration of metals and explosives, and to verify the presence or absence of explosives residues in background samples.

Energetic materials

Background Samples. Two of the background samples showed NG concentrations of about 3.6 mg/kg. The previous investigation found TNT to be present in all of the background samples (Thiboutot et al. 2003b). The explanation provided for the presence of TNT in the background samples collected during the initial investigation was that they had become contaminated during shipping, handling, or sample processing (Thiboutot et al. 2003b). Handling samples with high concentrations of TNT in the same general area as those from background locations requires special precautions. This potential problem and the lack of TNT in the second set of background samples collected at the same locations support the cross-contamination theory. The highest concentrations of NG established by both investigations were for samples collected at the same background location. This sampling location was on the edge of the woods adjacent to the firing point on the WAT at a distance of approximately 75 m. This energetic residue was distributed at this location as a result of firing rockets that have either double- or tripled-based propellants.

Wellington Antitank Rocket Range. To characterize energetic residues in the impact zone, different sampling strategies were used for each of the investigations. During this investigation the area that appeared to have received the most live fire was treated as a single sampling location. This strategy included the non-vegetated areas around tanks 1 through 4, including the road and the strafed areas in front of and behind the tanks. During the initial investigation of this range, we collected composite samples within 1 and 2 m around each of the five tanks positioned along the access road. In both investigations, sampling was performed from the top 2 cm with stainless steel scoops. Consistent with the findings of the Phase II study, HMX concentrations were higher than any of the other energetic residues on this impact range. Moreover, both investigations established the same order of energetic residue concentrations: HMX > NG > TNT > RDX > 2-ADNT and 4-ADNT. As found previously at this site and on other antitank ranges, concentrations of TNT were generally two orders of magnitude lower than HMX (Jenkins et al. 1997, 1999, Thiboutot et al. 1998, Arel et al. 2002). The much lower concentrations of TNT than what would be anticipated based on the composition of Octol were attributed to fate and transport properties of TNT being different from properties of HMX (Jenkins et al. 1997b). NG was also present, showing a median concentration of 26 mg/kg (mean and standard deviation: 34±21 mg/kg) for the eight replicates of the samples around tanks 1 through 4. NG is present in the propellant for the M72 LAW rockets and the 84-mm rounds. NG that is not consumed during flight is dispersed upon detonation.

Both investigations obtained a profile sample in front of tank 2. The profile sample collected during the initial investigation went to a depth of only 10 cm and was collected about 1 m from the tank. In 2002 at this location the concentrations of HMX, TNT, and NG were greater at the 5- to 10-cm depth than in the top 2 cm, and the report recommended that a deeper profile sample be collected to further investigate this trend. The profile concentrations of HMX, TNT, and NG all showed a decreasing trend with depth. For HMX, more than a three-order-of-magnitude decrease in concentration was observed from the surface to a depth of 28 cm. HMX was not detected in the deepest interval sample (28-31 cm). TNT (and its breakdown products, 2-ADNT and 4-ADNT) and NG were detected to depths of 19 and 14 cm, respectively. HMX is the least soluble and the most recalcitrant of these three energetic compounds to degradation (Thiboutot et al. 1998a, Miyares and Jenkins 2000). Therefore, at this location the resistance to biological degradation seems to play a more important role than solubility with regard to fate and transport.

The sediment and water samples taken from the pools of water in front of these four tanks contained detectable levels of HMX and NG; however, TNT was consistently detected in the sediment samples only. The concentration of HMX in the sediments ranged from 9.0 to 640 mg/kg and in the water from 0.016 to 0.57 mg/L. Likewise, the NG concentrations in the sediments ranged from 8.0 to 110 mg/kg and in the water from 0.002 to 1.8 mg/L. These shallow pools of water contained several deeper pockets of water. Poor circulation between these pockets may account for the wide range of aqueous HMX and NG concentrations.

At the firing point on this range, samples were collected in front of and behind the firing line. Both investigations determined that the samples collected behind the firing line generally had the highest NG concentrations. During the initial investigation a single composite sample with an NG concentration of 11,000 mg/kg was collected between 0 and 2 m behind the firing line (Thiboutot et al. 2003b). For this investigation several samples were collected in this same general area. Three separate composite samples collected immediately behind each of the concrete firing pads had NG concentrations that ranged from 28 to 610 mg/kg. Duplicate composite samples taken from 1 to 2 m behind the firing line contained 4,200 and 6,600 mg/kg. Taking into consideration the different areas sampled, the findings are consistent between the two investigations. Overall, the NG decreased with distance behind the firing line, ranging from concentrations in the thousands of mg/kg near the firing line to tens of mg/kg at 50 m. This trend is consistent with other studies of firing points at antitank ranges (Pennington et al. 2002, Hewitt et al. 2004). Both investigations established the same concentrations of NG in front of the firing line. In addition, similar to behind the firing line, the concentrations decreased with distance. For example, surface samples collected along linear transects of 10, 20, and 50 m showed NG concentrations of 420, 65, and 14 mg/kg for the samples collected in 2002 and were 290 (mean of replicates), 77, and 20 mg/kg in the 2003 samples. The agreement between these two sets of sample results suggests that NG has not increased on the surface over the past year.

Profile samples were collected 10 m in front of and behind the middle of the firing line. In both cases NG was detected in the samples collected at the deepest

interval (63 cm). In front of the firing line, NG was still present at a depth of 57 cm below the surface; behind the firing line it was present at a depth of 63 cm. In both locations a mean concentration of 15 ± 5 mg/kg was established for the surface profile discrete samples. Based on the average surface concentration in both of these areas, the NG concentrations had decreased by approximately four orders of magnitude from the surface to the deepest profile sample. Even though this is a large decrease in concentration, the presence of NG at these depths suggests that migration is rapid and/or that microbiological activity is limited. Laboratory studies have reported the half-live of NG to be less than a day (Jenkins et al. 2003).

New Castle Hand Grenade Range. This is a new range that has been in use for almost two years. Range control stated that 2459 M67 hand grenades were detonated on this range since its opening, meaning approximately 1200 grenades were fired per year. The M67 hand grenade contains 183 g of Composition B (60 percent RDX and 40 percent TNT). We can then extrapolate that 270 kg of RDX and 180 kg of TNT were detonated in the past two years. There were a few trace-level concentrations of TNT (<0.005 mg/kg) detected in the samples collected during this investigation, and a single trace-level (0.010 mg/kg) detection of RDX in the samples collected during the previous investigation. This confirms that when hand grenades are fired under a high-order detonation process, very little contamination occurs. Much higher concentrations of these two energetic residues would be present if even a single hand grenade had undergone a low-order, or partial, detonation during a training exercise or blow-in-place operation (Jenkins et al. 2001, Hewitt and Walsh 2003).

40-mm New Castle Rifle Grenade Range. Composite samples were collected in rectangular areas (approximately 30 × 25 m) near two sets of targets that were positioned at two distances from the firing point. Near the first set of three targets, between 100 and 130 m from the firing point, RDX, NG, and 2,4-DNT were detected at low concentrations (<0.2 mg/kg). The previous investigation also established the presence of NG and 2,4-DNT at or below 0.2 mg/kg in this general area. Since this range is next to the New Castle Hand Grenade range and was constructed at the same time, the presence of NG and 2,4-DNT was attributed to a pre-existing range condition (Thiboutot et al. 2003b) since this area could have been used for both grenade and artillery firing. Farther downrange at a distance between 170 and 200 m from the firing point, HMX, RDX, and NG were detected. Near the target on the left side of the range at this distance, the concentration of RDX was 0.5 mg/kg. The detection of RDX on this range is consistent with the main charge in 40-mm rifle grenades, which is Composition B. Moreover, since RDX had not been detected previously, this energetic residue may have just started to build up on the surface over the past year.

Blow-in-place of two 84-mm antitank rounds. Prior to the demolition operation, the surface samples from within the ordnance disposal bunker showed that HMX, NG, TNT, and two of its breakdown products, 2-ADNT and 4-ADNT, were present. In these pre-demolition samples the HMX concentrations did not exceed 0.6 mg/kg, TNT was less than 0.08 mg/kg, and NG did not exceed 20 mg/kg. The blow-in-place of the two 84-mm rounds formed two small blackened craters (70 cm in diameter, 20 cm deep). HMX, TNT, and NG were detected in every post-detonation sample. In addition, RDX was present in the crater

samples and in one of the duplicates collected within the 1-m-diameter circle. Overall, HMX ranged from 30 to 120 mg/kg (median: 82 mg/kg), TNT ranged from 1.8 to 34 mg/kg (median: 6.1 mg/kg), and NG ranged from 9.7 to 110 mg/kg (median: 38 mg/kg) in the post-detonation samples. The two-orders-of-magnitude increase in the concentrations of HMX and TNT can be attributed to the Octol in the rounds. Since similar levels of energetic residues were found in both craters, both rounds probably contributed to the build-up of energetic residues. The much smaller increases seen for NG indicate that this energetic compound was efficiently consumed. Residues of RDX can be attributed to the blocks of C4 used for this demolition operation.

Blow-in-place of 500-lb bomb. The samples that were collected prior to the detonation of the 500-lb bomb showed the presence of trace quantities (<0.05 mg/kg) of RDX, TNT, and TNB. Previously collected samples in a different part of this range showed the presence of trace quantities of RDX and 2,4-DNT (Thiboutot et al. 2003b). Following the blow-in-place of this bomb with three blocks of C4, NG was detected in every surface sample and trace quantities of RDX and TNT were sporadically detected. These findings show that the energetic compounds in the main charge in the bomb and the demolition blocks of C4 were efficiently consumed in the detonation. NG, which ranged from 0.014 to 3.4 mg/kg in the post-blast samples, presumably came from the fuze or booster of this bomb.

Burning Pads. In 2002, two burning locations were sampled and showed residues of 2,4-DNT in all samples in concentrations up to 32 mg/kg. Other target analytes, 2,6-DNT, TNT, RDX, and tetryl, were also detected. No NG was detected, indicating that only single-based propellant was burned in the two locations. The sampling conducted in 2003 encompassed four burning locations. For Locations 1 and 2, we can see a clear trend for 2,4-DNT, which goes from 17 to 491 mg/kg around Pad 1A and from 32 to 57.7 mg/kg around Pad 1B. Location 2B presented lower concentrations in 2003 for 2,4-DNT. In general Location 3 presented low levels of contamination, while Location 4B presented 60 mg/kg of 2,4 DNT and small concentrations of NG; therefore, double- or triple-based propellant might have been burned on this specific location. The highest concentration detected was at Pad 1A with 491 mg/kg, then Pad 4B at 60.4 and Pad 1B at 57.7 mg/kg of 2,4-DNT.

Metals

The concentration and distribution of heavy metals were not clearly delineated in the 2002 study. We wanted to learn more about metals mobility and fate in the environment and about their evolution in concentrations with time, one year later. To learn more about metals mobility and leachability, depth profiles were collected at two locations in the antitank range, and leaching tests (EPA 1996) were conducted (EPA 1311) on heavily contaminated samples.

Background Samples. Metals were analyzed in all background samples collected in 2003 in order to obtain a higher number of representative background sample and extrapolate a better mean background value (MBG) than achieved in 2002. Mean background values were calculated by adding the

average value obtained for all samples to twice the standard deviation attached to the mean value. We are aware that this method is not a valid approach from a purely statistical point of view. However, it is a simple means to measure trends in the firing range and highlight the analytes that will have to be monitored in the long term in the live-fire area where metals are accumulating. Results were also compared to the Industrial Soil Quality Guideline (ISQG) published by the Canadian Council of Ministry of the Environment (CCME), criteria selected for comparison as more applicable to the context of training areas (www.ccme.ca).

Wellington Antitank Range Samples. In Phase II, Cu, Ni, and Zn exceeded the ISQG in all samples in the target area. The following analytes exceeded the MBG: Ag, Ba, Bi, Ca, Cd, Cr, Mo, Pb, Sb, Sr, and W. In the FP, no analytes exceeded the ISQG, while only a few exceeded the mean background value, usually behind the FP (Cd, Cu, Mo, Ni, Pb, Sn, and Sr). In 2003, 107 samples were collected in the antitank range. In the target area, many soil replicates were collected to assess the variation between field replicates using multi-increment composites in the large sampling area. By comparing the results obtained for all analytes for all sets of replicates, we observed very good reproducibility between field replicates. Concentrations of metals showed a statistically significant correlation between field replicates. This indicates that our sampling approach led to representative results for metal analytes.

Target Area. Results obtained in the target area demonstrated that the soils were impacted with Cu, Ni, and Zn at levels higher that the ISQG, respectively, for 100, 50 and 10 percent of all samples collected. Copper was the most problematic analyte, with levels as high as 25 times the ISOG. Many other metal analytes accumulated over the MBG concentrations and should be monitored in the future. The following metal analytes were over the MBG in the target are (within brackets: percentage of samples higher than the MBG): Ag (100 percent), Ba (70 percent), Bi (100 percent), Cd (100 percent), Cr (90 percent), Mo (100 percent), Pb (100 percent), Sb (100 percent), and Sn (100 percent). Results are comparable to those observed in 2002. In both campaigns, levels of concern of Cu were found in all target samples and Ni, while Zn exceeded the ISQG in many samples. Eight sediment samples were collected in ponds located between targets one and two and two and three. This set of samples had high concentrations of several metals of concern. In particular, the levels of Cu were very high, the highest being 10,600 mg/kg, which is almost a hundred times the ISQG. In addition, As, Cr, Ni, Pb, and Zn exceeded the ISQG. Finally, almost all other analytes of concern were higher than the MBG. The ponds are formed by accumulation of runoff water from nearby targets. Build-up of contaminants is taking place in these locations.

To assess the fate of antitank range munitions-related contaminants, a pit was dug in front of Tank Target 2 for profile sampling. Levels of Cu higher than the ISQG were obtained from the surface layer to a depth of 20 cm with successively decreasing levels to a layer where the concentration was higher than the MBG at a depth of 19–26 cm. The concentrations became equal or lower than the MBG at a depth of 31 cm. All parameters higher than the ISQG or MBG showed a similar trend, with decreasing concentrations from the surface to depth, reaching values equal to or lower than the MBG at a depth of approximately 20 cm.

Firing Position. In 2002, only four samples were collected in the FP area. High levels of propellant residues were detected in these samples; therefore, further sampling was conducted in this area in 2003. Results obtained in 2002 indicated that a few metal analytes exceeded the MBG (Cd, Cu, Mo, Ni, Pb, Sn, and Sr) without reaching CCME ISQG concentrations. This was confirmed in 2003, with detections slightly over the ISQG for Cu and Ni in two samples out of 34. The concentrations of two samples that were over the ISQG were not consistent with their soil replicates; therefore, the replicates' means did not exceed the ISGQ.

New Castle Rifle Grenade Range. Only one concentration over the ISQG for Cu was observed, which was a very localized and small impact. Four other analytes were detected at concentrations slightly higher than the MBG (Pb, Sn, Sr, and Tl).

New Castle Hand Grenade Range. When we compare the results from 2002 and 2003 for the same locations for all analytes, the parameters that were of concern in 2002 (Cu, Pb, and Zn) exhibit still higher levels in 2003. Both Cu and Zn levels have increased by approximately 30 percent. Copper concentrations increased, while still under the ISQG. Pb concentrations were stable. Levels of Sn have increased by a factor of 20 between the two sampling events. The hand grenade range presented levels of concern of Zn on the entire surface of the range until 40 m away from the bunker and 5 m each side of the bunker. This means that an overall surface of 65 m by 40 m contains levels of Zn higher than the ISQG and levels of Cu, Pb, and Sn higher than the MBG.

When we compare the results obtained in the Gagetown and Shilo hand grenade ranges (Thiboutot et al. 2001, Ampleman et al. 2003), we observe that levels of heavy metals are lower in Gagetown than in Shilo. Gagetown range is two years old, while the Shilo range has been in operation for more than 20 years. Nevertheless, the same parameters of concern arose in both ranges: Cu, Pb, and Zn. In Shilo, Cu levels are approximately 10 times higher (ranging from 91 to 779 mg/kg), and Zn results are approximately 4 times higher (ranging from 1180 to 2400 mg/kg). Higher levels of Cd were also detected in Shilo, which might be attributed to the use of German grenade on this range. The results obtained in the Shilo and Gagetown hand grenade ranges are logical, complementary, and related to the intensity of the past training conducted at each range.

Blow-in-Place Locations. Metals were analyzed prior and after the BIP of two types of items to verify if BIP can lead to detectable augmentation of heavy metal analytes in the BIP area.

Blow-in-place of two 84-mm antitank heat rounds. Two 84-mm rounds were blown in place by the EOD teams at the BIP bunker near the antitank range firing point. Four soil samples were collected in the bottom of the pit before and after the detonation. In addition, two samples were collected in each crater after the BIP. The results showed that three metal analytes were detected over the MBG in the bottom of the pit: Cd, Cu, and Sn. If we compare results before and after the detonation, the concentrations remained stable with the exception of Cd, Cu, and Sn, where higher levels were detected after detonation of the rounds.

Blow-in-place of 500-lb bomb. Soil samples were collected before and after the detonation of a 500-lb bomb in the Hersey Range. In the pre-blast samples, some results over the MBG were detected for Ba, Cd, Cu, Mn, Pb, Sn, and Sr. The highest result was for Pb at 208 mg/kg. These high concentrations might result from the leaching of metal particulates from the bomb casing if the casing was compromised or from past firing activities in the Hersey Range. The parameter exceeding the MBG were also detected over this limit in most samples collected last year in the Hersey Range, thus supporting the second hypothesis. The following analytes (percent increase) were higher post-blast than pre-blast: Al (33 percent), Ba (25 percent), Be (50 percent), As (33 percent), Ca (25 percent), Co (60 percent), Cr (100 percent), Fe (100 percent), Li (80 percent), Mg (100 percent), and Mn (30 percent).

Burning Pads. In 2003, four burning location were sampled compared to two in 2002. In 2002, the following metals were of concern: Pb and Sr. This was expected, considering the fact that some gun propellant bags contain Pb as a lubricating agent for the gun barrel. Strontium might come from the burning of flares on the concrete pads. These trends were confirmed in 2003 with the accumulation of much higher levels of Pb. Values near 60,000 mg/kg were measured around the concrete pad number 1. Levels of Sr also increased to almost 6,000 mg/kg. Concrete pads 1 and 2 have apparently been used more extensively than other pads and presented levels over the ISQG for Pb.

Vimy Small Arms Range. Samples were collected both in the target area and in the firing line positions to assess the contamination by heavy metals on the firing lines. The following parameters exceeded CCME ISQG: Pb, Cu, and Sb. This is directly related to the small arms munitions composition, where the casing is made of Cu and the filling is made of Pb and Sb. The Pb contains 2 percent by weight of Sb to give more stiffness to the composition (Interstate Technology and Regulation Council 2003). Concentrations of Pb detected from 2002 to 2003 increased by factors varying from 1.5 to 234. The ratio between Sb and Pb was smaller than 2 percent. The depth samples also contained high levels of heavy metals. Finally, the residential soil quality guideline (RSQG) for Pb has been taken into account for samples collected in the firing lines, since military people lie down on the soil surface while firing their weapons. When compared to the RSQG, concentrations of Pb were higher than the threshold at the 100- and 300-m lines.

TCLP Testing

Based on the high levels of Pb detected in 2002, leaching tests were conducted on the soils collected both in the small arms range and in the propellant burn area. The Environmental Protection Agency (EPA) Toxicity Characteristic Leaching Procedure (TCLP) Test Number 1311 (EPA 1996) was used. This is a stringent test. In the U.S., when soil samples exceed 5 mg/kg of Pb, the soil must be managed as hazardous waste. The TCLP is designed to mimic condition of long-term leachability of heavy metals (EPA 1992, 1996). TCLP results were compared to EPA Regulatory levels for leachates, Environment and Fauna Quebec Regulatory Levels for Leachate Testing of Dangerous Goods and Transport Canada TCLP levels for hazardous materials. Soils are not regulated by

TCLP in Canada, only dangerous goods are. However, results of the TCLP on heavily contaminated soil samples represent a means to verify their long-term leachability potential.

Vimy Small Arms Range. Results of the TCLP test on the small arms range samples indicated that Pb had the potential for leaching to the groundwater table with levels as high as 1440 mg/kg of dissolved Pb in the soil leachate. Interestingly, the highest concentration was observed for a depth sample. No threshold criteria exist for Sb, but levels of 3 mg/kg were detected in some leachates, indicating that Sb is leachable as well.

Burning Pads. Results of the TCLP tests on the burning pads areas showed the same tendency for Pb as observed in the small arms range, but to a lesser extent, with concentrations of Pb as high as 428 mg/kg in the soil leachate collected around Pad 1B. Results obtained for the leachates correlated with those obtained in the soil samples. Higher levels of Sr were observed in the soil samples and were reflected in the leachate results, where a concentration of 13 mg/kg was obtained for the soil leachate coming from the Pad 3A. Both Pb and Sr detected in soil around the Gagetown burning pads possess long-term leachability potential.

Conclusion

The collection of supplementary background samples demonstrates that the detection of TNT observed in 2002 was caused by cross-contamination between samples. As per the sampling strategy, a systematic approach to building a composite sample for a larger area has proven to be effective. Two benefits are the reduction of the number of samples that need to be processed and analyzed and the establishment of a more representative average concentration.

In the WAT target area, surface soils are mainly impacted by HMX, Cu, Ni, and Zn. In the profile samples, HMX, TNT, and NG decrease with depth and are still detectable near or at the bottom of the profiles. In the future, deeper profile samples should be obtained to further investigate the migration of energetic residues. A progression with depth is also observed for heavy metals. Global results for all metal analytes indicated that levels of concern are limited in the top 20 cm of surface soil.

Energetic residues and heavy metals in sediment and water samples from ponds in the target area are detected at higher concentrations than in the surrounding surface soils. Variable concentrations (with more than one order of magnitude) of energetic residues are detected in the surface waters, demonstrating that the ponds are non-homogeneous. In the future, co-located water and sediment samples should be obtained to help explain the wide range of concentrations within contiguous bodies of water. These findings suggest that surface runoff should be controlled on antitank impact ranges to prevent off-site migration of munitions-related contaminants.

In the firing position, no metal analytes are detected over levels of concern. The firing leads to the accumulation of high levels of NG at the FP, with concentrations reaching peaks of 17,000 mg/kg (1.7 percent w/w). NG is detected in profile samples even at the deepest layer collected, which suggests that migration is rapid and/or that microbiological activity is limited. That can be explained by the fact that NG is embedded by nitrocellulose, is stable, and moves. Vertical migration of NG is demonstrated, and fate studies on propellant residues should be undertaken to learn more about their migration patterns.

Results at the New Castle Hand Grenade range demonstrate no evidence of energetic residues build-up. This confirms that when hand grenades detonate properly (i.e., high-order detonation), very little residue remains. The hand grenade range presented levels of Zn higher than the ISQG on its overall surface of 65 by 40 m. In the rifle grenade range only one sample exhibited a concentration over the ISQG for Cu, and a slight build-up (0.5 mg/kg) of RDX was observed near the targets. This may be attributed to munitions currently being used at this facility.

The BIP of two 84-mm rounds led to an increase in concentrations of Cd, Cu, and Sn and to the detection of traces of HMX and TNT. These findings support the contention that if the same location is used repeatedly for demolition operations, energetic residues and metals are likely to build up. For the BIP of the 500-lb bomb filled with Tritonal, no appreciable increase in the concentration of TNT was observed, which demonstrates that the operation was a successful high-order event. An increase in the concentrations of Al, Ba, Be, Co, Cr, Fe, Li, Mg, and Mn was observed after the BIP. This is the first documentation of the localized impacts of BIP operations on metals concentrations and should be confirmed with additional trials.

The main contaminants detected at BP locations are 2,4-DNT, Pb, and Sr. Leachate testing of the BP soil samples demonstrated that both Pb and Sr have the potential for migrating to the groundwater table. A decision was recently made to stop using these pads, which were judged inefficient. The surface soils around the pads should be collected and sent to an appropriate landfill.

In the SAR, Pb, Cu, and Sb concentrations exceed the CCME ISQG. We can see a progression between 2002 and 2003, with an increase in levels of Pb by factors varying from 1.5 to 234. The ratio between Sb and Pb indicates a higher leaching rate for Sb. In the 100- and 300-m firing lines, Pb concentrations were detected over the accepted CCME residential threshold. This situation should be examined from a human health perspective, based on the frequency of firing at these locations. In the sand stop buts, results indicate a potential for Pb to leaching to groundwater. The highest concentration is observed for a subsurface sample, which suggests that Pb species found in deeper layers are more soluble and are slowly moving to the groundwater.

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5 Characterization of Soil,
Vegetation, Surface Water,
and Sediment for
Explosives and Metals
Contamination at Cold
Lake Air Weapons Range
(CLAWR), Alberta, Phase II,
Final Report

This chapter is an abstract of the following published technical report:

Ampleman, G., Thiboutot, S., Lewis, J., Marois, A., Gagnon, A., Bouchard, M., Jenkins, T. F., Ranney, T. A., and Pennington, J. C. (2004). "Evaluation of the contamination by explosives and metals in soils, vegetation, surface water and sediment at Cold Lake Air Weapons Range (CLAWR), Alberta, Phase II, Final report," DRDC-Valcartier TR 2004-204, Defence Research and Development Canada-Valcartier, Quebec.

Introduction

Energetic materials are prominent components of munitions and weapons that can be found in war zones, at training ranges, and on production sites. During this decade, many needs have emerged related to identifying, quantifying, and eliminating energetic contaminants dispersed by munitions or present in explosives dumps, trials or destruction fields, firing areas, and production sites (Cragin et al. 1985, Jenkins and Walsh 1987, Fellows et al. 1992, Checkai et al. 1993, EPA 1993, Selim and Iskandar 1994, Jenkins et al. 1997a, 1997b, 1998a, 1998b, Thiboutot et al. 1997, 1998a, 1998b, 2000, 2002, Ampleman et al. 1998, 2000, Walsh and Ranney 1998a, 1998b, 1999, Brannon et al. 2000, Pennington et al. 2001, Walsh 2001, Walsh et al. 2001). Many Canadian Forces sites used as impact areas, training ranges, and demolition and open burning/open detonation (OB/OD) ranges, which were used to destroy out-of-specification materials, were

suspected of being contaminated with energetic constituents as described in the literature (Checkai et al. 1993, EPA 1993, Jenkins et al., 1997b, 1998a, 1998b, Thiboutot et al. 1997, 1998b, 2000, Ampleman et al. 1998, 2000, Brannon et al. 2000, Pennington et al. 2001, Walsh et al. 2001). High explosives used by both Canada and the United States generally contain either TNT (2,4,6-trinitrotoluene) or mixtures of TNT with RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine), HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine), or, for some older munitions, tetryl. Most of the air weapons contain TNT with aluminum (tritonal explosives). The most powerful weapons contain Composition B (TNT with RDX) or Octol (TNT with HMX). When UXOs are found on sites, they are often blown in place (BIP) using C-4, a mixture of RDX with a polymer. These BIP operations often spread explosives into the environment (Pennington et al. 2001). To evaluate the contamination of Department of National Defence (DND) sites, sampling and characterization of various ranges was performed over the last ten years. A protocol describing the different methods of sampling and the analytical chemistry was developed (Thiboutot et al. 1998a). This protocol was recently updated in collaboration with CRREL and is presently being reviewed under the auspices of the Technical Cooperation Program (TTCP) by the member nations (Canada, the U.S., the U.K., Australia, and New Zealand) in a key technical area (KTA 4-28) (Thiboutot et al. 2002). Research results to date have demonstrated that explosives exhibit limited aqueous solubility and are dispersed in a heterogeneous pattern of contamination. In the United States, concerted efforts have been made to develop methods of chemical analysis, to establish the best sampling procedures, and to understand the complex fate of explosives in the environment (Cragin et al. 1985, Jenkins and Walsh 1987, Fellows et al. 1992, Checkai et al. 1993, EPA 1993, Selim and Iskandar 1994, Jenkins et al. 1997a, 1997b, Walsh and Ranney 1998a, 1998b, 1999, Pennington et al. 2001, Walsh 2001).

The Cold Lake Air Weapons Range (CLAWR) in CFB Cold Lake was selected for the first research and development efforts to assess the environmental aspects of live-firing activities on an air base. CLAWR was selected as the result of a growing interest by 4-Wing following the characterization of CFB Shilo and also because Cold Lake is the largest air base in Canada. Being the largest and the most used area for air practice with live weapons, CLAWR is the area that is most representative and worthy of studying among air bases. The problems resulting from air bombing are completely different from those encountered on Army ranges. The weapons used are different in size and content. Low-order detonations of air weapons may result in high concentrations of explosives in the environment, as was seen in CFB Gagetown (Thiboutot et al. 2003). Furthermore, the Air Force uses rockets that contain ammonium perchlorate, a newly recognized contaminant that is extensively studied in the U.S. When these rockets hit the ground, some of them are not completely burned and can break into pieces following the impact with the ground, spreading ammonium perchlorate on the surface. Since this contaminant is ionic, it is highly soluble in water and may proceed rapidly to the groundwater.

The ultimate goal of this second phase of the surface characterization was to resample contaminated areas identified during Phase I and to better understand the global contamination related to explosives and heavy metals dispersed at the surface and in soil and vegetation, but also in surface water and sediments. The contamination patterns of surface soils around targets and across the ranges were re-evaluated in Alpha, Jimmy Lake, and Shaver River Ranges. The same

approaches and strategies used during Phase I were applied to resample Jimmy Lake and Shaver River Ranges. Furthermore, a statistical evaluation of the explosive concentrations was done in Shaver River Range. Background samples were also collected to assess the natural and anthropogenic contribution. In worst-case locations, vegetation samples were collected to assess phytoaccumulation and the potential risk for wildlife. Moreover, the remote areas were also visited and sampled mainly for metal concentrations. Finally, the quality of surface water and sediments was evaluated in Primrose Lake and Jimmy Lake by collecting surface water and sediment samples in both lakes. In total, 324 soil (including 100 discrete samples and 12 composite samples to realize the statistical analysis in Shaver River Range), 69 vegetation, 19 water, and 28 sediment samples were collected.

To better assess the contamination and characterize an area, an appropriate definition and understanding of the hydrogeological context of the site is required. Characterizing the groundwater quality, especially on large ranges, is critical because metals and energetic materials are mobile in sandy environments and may migrate to groundwater, presenting a threat to human health and to the environment. Groundwater flow has to be carefully assessed by determining its velocity and direction. The quality of the groundwater also has to be evaluated, since it may be used as a drinking water source by the base and occasionally for irrigation; groundwater quality is also important for sustaining aquatic ecosystems. Consequently, any contamination could impact human health and aquatic ecosystems. In fact, groundwater flowing under CLAWR discharges into Primrose and Jimmy Lakes and also into rivers such as the Shaver River. All are highly sensitive areas for wildlife and humans receptors. The first phase of the hydrogeological study was accomplished in February 2004. All of the results from this study will be reported in 2005. Many wells were drilled in February 2004, but groundwater samples were mainly collected in August 2004, since most of the wells were frozen in February. The second phase of this hydrogeological study occurred in November 2004, and results will be reported in 2005.

In this report, all of the surface work carried out during Phase II in August 2003 is described, and the results were compared with results obtained during Phase I to better assess the situation in the ranges. This study was performed within the context of growing awareness of environmental issues. The Director, Research and Development Branch, through DRDC-Valcartier, directed some of its resources to assess and develop expertise related to the environmental risks associated with explosive compounds, and this work was performed under the work breakdown element 12NY01, "Characterization of DND Sites Contaminated with Energetic Materials," which was sponsored mainly by 4-Wing with sampling of surface soils sponsored by the Strategic Environmental Research and Development Program (SERDP). All work was done in collaboration with U.S. Army Engineer Research and Development Center (ERDC) scientists from CRREL and EL under the umbrella of Canada DND-US DoD Test and Evaluation Program Cooperation under the Memorandum of Understanding (CANUSTEP-MOU). This joint venture was initiated to evaluate the fate of explosives in live-firing ranges under the auspices of SERDP, a major funding program in the U.S. DoD and was leveraged by both Defence departments. Defence Construction Canada (DCC) was responsible for hiring the analytical

laboratory, providing manpower and logistics, and making the link with range control personnel.

Range Description

4-Wing – Cold Lake, situated in the remote north-eastern corner of Alberta on the border with Saskatchewan, was opened in 1954 as an air weapons training base, a function that it still performs today. 4-Wing also takes care of the nearby CLAWR, one of the most sophisticated facilities of its type in the world. It is the only tactical bombing range in Canada and incorporates over 100 target areas with over 700 individual targets ranging from disused vehicles to dummy surface-to-air missile sites and airfields. CLAWR has been designated a supersonic range, with pilots able to fly their aircraft at that speed to an altitude as low as 30 m. The CLAWR is heavily used during the annual Maple Flag exercise, which brings together several NATO air forces for six weeks of intensive flying above the Cold Lake pine forests.

CLAWR covers an area of approximately 180 × 65 km and is approximately 54 km northeast of CFB Cold Lake at the junction of Alberta with Saskatchewan, having Primrose Lake as a boundary. This lake is used for commercial fishing and also serves as an area to approach the ranges. The four main ranges in CLAWR are Alpha and Bravo, which are part of the Primrose Lake Evaluation Range (PLER), and Jimmy Lake and Shayer River. Alpha and Brayo ranges are located, respectively, from south to north following the southwest shoreline of Primrose Lake, while the Jimmy Lake Range is located between Jimmy Lake and Primrose Lake. The Shaver River Range is remote to the lakes and close to the Shaver River. This range is mostly dedicated to live firing using 500-pound air bombs. All ranges in CLAWR contain several ground target complexes for bombing training. Both the Jimmy Lake and Shaver River ranges are licensed for live weapons using up to 2,000-pound general-purpose bombs and live firing of missiles. The Primrose Lake water zones are called drop zones Charlie, Delta, and Echo and are used to analyze the performance of multiple rocket launchers, e.g. CRV-7, or cluster munitions.

Experimental

Parameters Monitored and Analytical Methods

Soil and surface water samples were analyzed for metals and energetic materials, while vegetation and sediment samples were analyzed only for metals. Metals were analyzed by inductively coupled plasma/mass spectrometry (ICP/MS) by the external laboratory, Enviro-Test Laboratory (ETL) from Edmonton, Alberta. All of the parameters available by this method were included in the study. For soil and surface water samples, energetic materials were analyzed at DRDC-Valcartier using the high-pressure liquid chromatography USA EPA Method 8330, a method that can produce a 0.1-ppm detection limit (see http://www.epa.gov/epaoswer/hazwaste/test/pdfs/8330.pdf for a complete technical description of the HPLC method). The same method was used at CRREL to

analyze the samples for the statistical evaluation of the energetics in Shaver River Range. The HPLC method was preferred over the gas chromatography method recently published, since reproducible results with the GC/ECD method were difficult to achieve (Walsh and Ranney 1998b, Walsh 2001). In our study the HPLC method gave us a detection limit of 0.25 ppm for all analytes; this detection limit was reduced to 0.06 ppm when the sample extracts were concentrated in a Zymark apparatus, model Turbovap evaporator, produced by Zymark Corporation (Hopkinton, Massachusetts, USA). The reporting limits obtained for energetic materials in the present study were typically between 100 and 1000 ppb for soils, depending on the analyte. No vegetation samples were analyzed for energetic materials, since no explosives were detected in a previous study (Thiboutot et al. 2001, Ampleman et al. 2003).

Sampling strategies

During Phase I, soil, vegetation, and surface water sampling showed high concentrations for metals and explosives in Jimmy Lake and Shaver River Ranges. During Phase II, these two ranges were resampled to verify the results of Phase I. Jimmy Lake Range was evaluated using both circular and linear sampling strategies, while for Shaver River Range, only the circular strategy was applied, plus a statistical evaluation using 100 discrete samples. During Phase II, vegetation sampling that had been omitted during Phase I was accomplished in Alpha Range using the linear transect strategy. Moreover, the remote areas were visited by helicopter and sampled for metals. For the remote areas, at each location a different strategy was applied and will be described in this section. A total of 324 soil samples were collected, including 100 discrete samples plus 12 composite, 15 duplicate, and 12 background samples. Sixty-nine vegetation samples were also collected, including 11 duplicate and 19 background samples. Nineteen surface water samples including 2 duplicates and 28 sediment samples including 5 duplicates were collected during Phase II. The surface water samples were collected mainly in Primrose Lake and Jimmy Lake, but also in Shaver River, in remote areas, and in depressions/craters containing water in Alpha and Shaver River Ranges. Sediment samples were collected in Primrose Lake and Jimmy Lake. All 440 samples were analyzed for metals, while a limited number were analyzed for energetic materials (180 soil and 8 water samples).

Background soil samples are critical for establishing the anthropogenic contribution versus the natural contribution for all metal parameters. Background composite samples were collected randomly, in circles approximately 10 m in diameter in different locations inside and outside the base. A minimum of 30 subsamples were collected to form each background sample. A statistical analysis was conducted to identify a mean background concentration and to define a limit for a value that can be considered normal. Values at the extremities of the lognormal curve were identified. The limits were chosen for a probability of 97.72 percent (two times the standard deviation). The probability of finding a result with a value higher than this limit is 2.28 percent. When the analytical laboratory did not detect metals, we used a value at half of the detection limit for the data analysis.

The usual strategy for soil sampling was based on systematically sampling around a representative number of targets in ranges and also around hot spots (broken casings, UXOs, debris, etc.). Usually, surface soils were collected at a depth of 0-5 cm. This strategy was used in previous studies on antitank ranges, which showed distinct patterns of contamination around targets (Thiboutot et al. 1998b). This strategy was used mainly in remote areas. In Bravo Range, only a few samples were collected, and most of them were background samples. In Alpha Range, the linear transect strategy was used to collect the vegetation samples. As performed during Phase I (Figure 5-1), this approach was used to evaluate whether the level of contamination by metals or energetic materials followed a pattern with distance from the target in the ranges. If firing activities led to the accumulation of contaminants in soils or vegetation, higher concentrations should be found around targets. Therefore, composite samples were collected at distances of 20, 40, 60, 100, 120, and 140 percent of the distance from the entrance of the range to the target. Most of the time, an access road for maintenance and clean-up went directly to the targets in the middle of the ranges. The road was used to build transects (right and left of centerline) perpendicular to the road. Transects were fixed with the help of the global positioning system (GPS). For example, at 20 percent of the distance, we collected on each side of the road walking perpendicularly to the road using a GPS to keep on a straight line. A minimum of 20 surface subsamples at 0- to 2-cm depth were collected to build each composite sample. The composites were built by walking 100-200 m. At hot spots or other artifacts of interest, compositing of a minimum of 20 discrete samples was used. This strategy was used in the strafing area of Jimmy Lake range except that the 40 percent corresponded to the target area (Figure 5-2). Three to four sets of poles held targets for strafing in this range. Composite soil samples were collected behind three targets in transects that were split into A and B sections as illustrated (Figure 5-2). Transects were parallel to targets at distances of 20, 40, 60, 80, 100,120, 140, and 160 percent of a 150-m range. The soil samples collected in this range were composed of fine-grained sand and were collected in transect 0-100 percent. Samples of vegetation were taken at 20-60 percent and at 120-160 percent beyond the 150-m length of the range.

In the bombing area of Jimmy Lake and in Shaver River Ranges, the circular sampling strategy developed during Phase I was applied, consisting of sampling around targets by compositing samples taken in a circular pattern. This strategy, based on the circular sampling used at CFB Shilo, was used for specific target evaluation. The strategy was modified to adapt to the specific context of air-toground targets and was designed to allow a comparison of the relative concentrations in front of and behind a target. A semi-circular pattern was used to collect composite samples at specific distances from the targets (Figure 5-3). Twenty-six (26) soil samples were collected around targets, one within each of the cells around the target. Three circles located at 10-, 30- and 50-m radii of the target define these cells. Two composite samples (A1 and A2) were collected in hemispheres of the first 10-m-diameter ring (front and back of target). Eight equalsized rectangles were sampled between 10 and 30 m, and 16 between 30 and 50 m. Twenty or more increments were collected to build 0.8-1.5 kg composite samples. In Jimmy Lake Range, an old truck was used as the target, while a tank was used as the center of the circular strategy in Shaver River Range. In this range, air dropping of 250-, 500-, and 1000-pound high-explosive (HE) bombs at a stationary target is done on a regular basis. Significant explosive concentrations

had been measured during Phase I. For this reason, the circular approach was used to verify that the concentrations were of the same order of magnitude, even with range tilling performed regularly. As for the other ranges, the surface was covered with fine-grained sands.

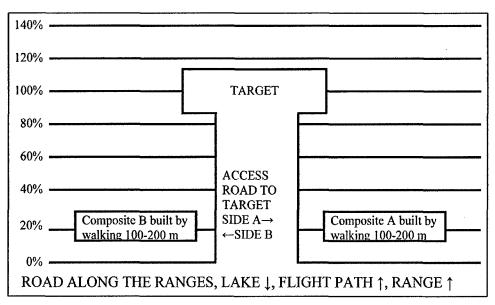


Figure 5-1. Schematic of the linear sampling strategy

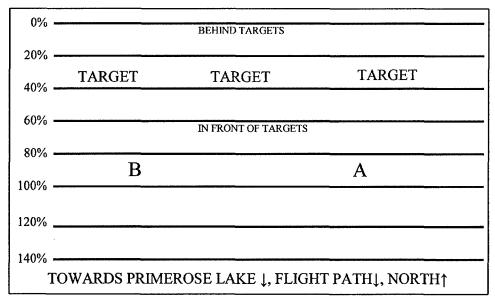


Figure 5-2. Modified linear strategy in Jimmy Lake Range

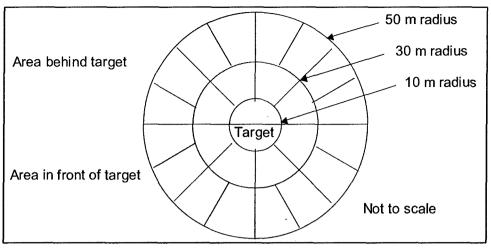


Figure 5-3. Schematic of the circular sampling strategy

The purpose of the sampling experiment conducted at the Shaver River Range was to understand the distribution of energetic residues at an Air Force bombing range in order to optimize the sampling strategy for collecting representative surface soil samples at these types of ranges. The emphasis was on surface soils because residues of energetic compounds are deposited as particles at the surface. These surface residues are the largest source of constituents for potential migration off site. To provide a reliable estimate of the mass of these residues at various locations on ranges, samples must represent these areas within an acceptable level of uncertainty. The level of uncertainty that would be acceptable is site specific. Our objective is to provide some guidelines to enable a selection of the sampling and subsampling protocols that can provide a specific desired level of confidence.

To achieve that goal, a $10-\times 10$ -m area was selected about 15 m from a bombing target in B-1. Four 30-increment composite surface soil samples (0-2.5 cm) were collected by two individuals using the random walk method. Surface soil increments were collected using stainless steel scoops, because the soils were coarse grained and not sufficiently cohesive to allow the use of a core sampler. Composite samples were placed in 32-oz glass jars in a cooler.

The $10-\times 10$ -m area was subdivided into one hundred $1-\times 1$ -m grids using wooden sticks. Within each grid, a discrete surface soil sample (10-50 g, 0- to 2.5-cm depth) was collected by several individuals at random positions using metal scoops. These discrete samples were placed in 4-oz amber glass containers. Both the $10-\times 10$ -m area composite samples and the discrete $1-\times 1$ -m grid samples were shipped to CRREL and analyzed with the protocol previously described.

Wherever vegetation samples were collected, the method consisted of building composite samples of indigenous living plants by randomly cutting various types of plants. A minimum of 20–30 sub-samples of mixed vegetation material were collected to build the different vegetation samples around targets and in transects. Only the upper parts of the plants (without roots) were collected, since grazing animals rarely eat the roots of the plants. Metals could bio-accumulate

either in the upper plant system or in the roots, depending on the solubility of the metals.

For surface water samples, the strategy consisted of collecting at 10 and 13 locations in Jimmy Lake and in Primrose Lake, respectively, and noting the GPS locations. Jimmy Lake is much smaller than Primrose Lake. Surface water was also collected in two craters formed by detonations, one in Alpha Range and the second in Shaver River Range. Sediment samples were also collected in Jimmy Lake and in Primrose Lake using a manual grabber. Excess water was removed by decantation, and the sediment was transferred into polyethylene bags that were frozen and kept in the dark until analyzed.

Finally, six sites were sampled in the remote areas using a helicopter. Many of these sites were highly vegetated and very wet. Sometimes collection of water samples only was possible. In these instances, water samples were collected by standing on the Heli-skids. No energetic materials are used in the remote areas, so the analyses were to determine metal concentrations. Usually, wooden targets or existing infrastructure such as old gas wells are used in the remote areas for aiming practice, laser pointing, etc. Inert practice bombs and rockets were found at two sites. In all of these sites, since our flying time was limited, only targets or infrastructures were sampled using the compositing approach. Efforts were made to collect soil, vegetation, and water when possible at each site. Site E-301, which was new and had never been used before, was considered as background for our study.

Results analysis

Our approach consisted of comparing all of the metals results to background values, then to the Canadian Council of Ministers of Environment (CCME) Agricultural Soils Quality Guideline (ASQG), and finally to the Industrial Soil Quality Guideline (IndSQG) (for a table of the water, soil, and sediment quality health risk based threshold criteria, see http://www.ccme.ca/assets/pdf/e1_062.pdf). Even if the Department of National Defence (DND) properties are not dedicated to agriculture, the ASQG represents the first official threshold value. Concentrations exceeding the ASQG can raise important questions for the management of the sites. This is particularly true for sites such as WATC Wainright, where cows are allowed to graze in the DND properties during summer. The same rationale can be applied to the IndSQG, since the DND properties are not industries, but having concentrations higher than the IndSQG can suggest a need for the DND to find and apply solutions for due diligence.

The mean background value for each parameter was the mean of all collected background sample values for that parameter. When results lower than detection limits were encountered for specific parameters, half of the detection limit for that parameter was used for calculating the mean value. The results obtained in training areas were compared to the mean value of the background, to which was added twice the standard deviation. This allowed the selection of results having values greater than the background means, while being representative. Results are presented for each parameter instead of per sample to facilitate the analysis of trends for each parameter. For metals that were not included in the CCME list,

results were compared to the mean values added to twice the standard deviation of all soil backgrounds samples. For vegetation, no CCME criteria exist, so results were compared to the mean values added to twice the standard deviation. For the surface water samples, the CCME Aquatic Life Threshold Criterion is the most appropriate value to use (see http://www.ccme.ca/assets/pdf/e1_062.pdf). For sediment samples, all of the parameters were compared to the CCME Interim Sediment Quality Guideline (ISQG) and to the CCME Probable Effect Level (PEL), which is more permissive than the IndSQG. In the following discussion, values indicated as higher than background are higher than the mean plus twice the standard deviation.

During Phase II, 324 soil, 69 vegetation, 19 surface water, and 28 sediment samples were collected in August 2003. Analyses for the following metals were conducted on all samples: Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mo, Ni, Se, Ag, Sr, Tl, Sn, V, and Zn. Soil, water, and sediment samples were also analyzed for Hg and U. Vegetation and surface water were also analyzed for the following: Al, Ca, Fe, Mg, Mn, K, Na, and Ti. Only surface water was analyzed for Li. Since plants were not washed, results include metals bio-accumulated and deposited on plant surfaces. Analyzing leachates to discriminate between metals in and on plants was not judged necessary, since wildlife ingest both.

Out of the 324 soils samples, 180 samples were analyzed for energetic materials. Eleven parameters were screened for, including the most common explosives, RDX, HMX, and TNT, using the HPLC method. Analyses for energetics were done at CRREL for the samples collected in the statistical evaluation and at DRDC-Valcartier for all other samples. Both labs used the RP-HPLC SW 846 Method 8330 with a typical reporting limit of 100 ppb for all analytes except for DNB, tetryl, and PETN, for which limits were slightly higher, at 200, 100, and 500 ppb, respectively. The detection limits for all analytes varied from 16 to 600 ppb. For the purposes of this report, we can consider that energetic compounds fall into two classes, those related to propellants and those related to high explosives. Nitroglycerine (NG), dinitrobenzene (DNB), dinitrotoluene (DNT), and trinitrobenzene (TNB) are either major ingredients or impurities in various types of propellants such as those used in rocket motors. TNB can also be an impurity of TNT, since benzene can be an impurity of toluene in the nitration to TNT. Usually, rockets use either double-based propellants composed of nitrocellulose and nitroglycerine or a thermoset polymeric matrix based on hydroxylterminated polybutadiene containing ammonium perchlorate as the oxidizer. Perchlorate analyses should be performed in ranges to evaluate impacts by this chemical. However, these analyses are costly and will be performed only for groundwater samples that will be collected during the hydrogeological study. The single-based propellants also contain DNT as a plasticizer and impurities such as DNB and TNB coming from the synthesis of energetic materials starting from toluene-containing benzene as an impurity.

Range sampling methods

The Alpha Range, located in front of Primrose Lake, is roughly 1.0 km long. This range was covered with grasses growing in fine-grained sand. Mainly vegetation samples were collected in this range since these were lacking in Phase I.

Vegetation samples were taken in front of the tank target and in front of the strafing wall, and background samples were collected at the boundaries of the range. Linear sampling for vegetation was also performed along transects (100 m each side) in front of the target going uprange at distances of 0, 200, 400, 600, 800, and 1000 m (Figure 5-1). No soils were collected and 22 vegetation samples were collected, including 4 background samples. No energetic analyses were performed in this range since the concentrations of explosives determined during Phase I were ≤ 1 ppm. A surface water sample was collected in a small puddle 50 m away from the tank target. In Alpha Range, a total of 46 soil samples and 5 vegetation samples were collected.

The Bravo Range is also located in front of Primrose Lake and is composed mainly of sandy soil with little vegetation. The range was freshly tilled when we arrived on site, and many concrete bombs were lying on the ground close to the target. Since the vegetation was very scarce and the site looked very clean, vegetation was sampled 70 m in front of the target (two samples, one right, and one left of the target). Background vegetation and soil samples (3 vegetation and 3 duplicates, 1 soil and 1 duplicate) were also collected. No energetic materials were analyzed in this range. No surface water samples were collected in Bravo Range.

The Jimmy Lake Range is located between Jimmy Lake and Primrose Lake. In Jimmy Lake Range, the bombing circle and the 20-mm strafing areas were sampled as illustrated in Figures 5-2 and 5-3. The practice target was used for concentric circular sampling (Figure 5-3), and the linear sampling strategy was used for the 20-mm firing range (Figure 5-2). For the bombing circle, 30 soil samples including 4 duplicates were collected in the circular sampling, while one vegetation sample was collected. Two vegetation samples were collected around the bombing circle and used as background samples. For the strafing areas, composite soil samples were collected in transects that were split into A and B sections (Figure 5-2). Transects were perpendicular to the direction of flight (west to east) and were placed at 20, 40, 60, 80, 100, 120, 140, and 160 percent of a 120-m range, the 40 percent transect being at the target locations. This strategy was used to detect any progression of the metal concentrations from behind to the front of the targets. In the strafing area, 14 soil samples including 2 duplicates were collected between 0 and 100 percent. In addition, 15 samples of vegetation including 3 duplicates were taken at each transect except at 80 and 100 percent, where no vegetation was present. The soil samples collected in this range were composed of fine-grained sand. A total of 44 soil samples and 18 vegetation samples were collected in this range. Energetic analyses were performed only on samples collected in the bombing area using the circular strategy, since the strafing area is not supposed to contain energetics.

Shaver River Range is located close to the Shaver River and is remote from Jimmy Lake. In Shaver River Range, air dropping of 250-, 500-, and 1000-pound HE bombs at stationary target is done on a regular basis. Again, the circular strategy was applied as performed during Phase I (Figure 5-3). As in the other ranges, the surface was covered with fine-grained sands. In Shaver River Range, 33 soil samples including 6 duplicates and 1 surface water sample from a crater close to the target were collected. Three soil samples were collected as background samples. No vegetation samples were collected, since no vegetation was present in

the bombing area. Energetic analyses were performed on all the samples collected in this range. Furthermore, 100 discrete soil samples were collected in front of the target in a grid of $100\text{-}\times1\text{-m}^2$ minigrids to evaluate the statistical dispersion of the explosives. Moreover, four composites were built to assess the heterogeneity by collecting soil samples randomly in the grid. Analyses focused on energetic materials, since this range was used mainly for live firing. Since the area surrounding the target position at the Shaver River Range is often tilled to minimize the vegetation and reduce the chance of the live-fire activities initiating a forest fire, the area was resampled to verify the effect of the tilling and heterogeneity on the results.

Eight surface water samples were collected in Primrose Lake, in Jimmy Lake, and in the Shaver River to evaluate the quality of surface water. Out of these, 6 were analyzed for energetic materials. In Jimmy Lake, the 3 water samples and the 12 sediment samples including 2 duplicates were collected using a small rowboat, while in Primrose Lake a motorized boat was used to collect the 4 surface water samples and the 16 sediment samples including 3 duplicates. Moreover, a last surface water sample was collected at the mouth of the Shaver River. No explosive analyses were done with the sediment samples. All the surface water samples were analyzed for metal, including the sample collected at the mouth of the Shaver River. Concentrations for each parameter were compared to CCME aquatic life in freshwater criteria when available or to the CCME drinking or irrigation criteria. The metal concentrations in sediment samples were determined and compared to the IndSQG.

Two days were needed to visit and sample six sites in the remote areas. The first visited site was C-295, a very wet airstrip where wooden targets were located. Surface water could only be sampled by standing on the Heli-skids at this site. No energetic materials are used in the remote areas, so most of the analyses were done to determine only metal concentrations. Most of the sites were highly vegetated and very wet. Efforts were made to collect soil, vegetation, and water when possible at each site. The second site was C-284, where old oil wells were used as laser pointing targets. At this site, two big metal reservoirs and four oil rigs were located. Two surface water samples were collected in small puddles; four vegetation and four soil samples were collected around the two reservoirs, in the middle of the range, and also around the oil wells. The third site was C-314, which was a small island used as a target in Primrose Lake. In the middle of the island, soil and vegetation samples were collected around a small wooden target and also in the areas right and left of the target. Three vegetation samples and two soil samples were collected and were named A, B, and C, B being around the wooden target. The fourth site was A-387, another airstrip with a wooden target where planes coming from the lake aimed. In this site, we collected only four vegetation samples in circles A, B, C, and D, B being around the target. The second day, we visited site F-332, a small hill surrounded by a lake. Much rocket debris was seen at this site. Two vegetation and two soil samples were taken on the left and right sides of the area. Just beside site F-332, a minute flight away, we landed to collect two water samples in the airstrip. Finally, the last site was E-301. This site was new, had never been used before, and was highly vegetated. We sampled around two intact wooden targets at this site. Samples A and B were collected beside the helicopter, and C was collected a little farther away (10 m). Three vegetation samples and three soil samples were

collected in A, B, and C. One surface water sample was collected in a small river surrounding the site. These samples were considered background.

Results and Discussion

For Phase I no major environmental impacts related to the training activities were identified. In soils the accumulation of some heavy metals associated with ammunition was observed in some parts of ranges, but concentrations did not reach levels of concern. Phase I results clearly demonstrated no major problems associated with soil contamination except in a few locations, such as Jimmy Lake and Shaver River ranges, which were resampled during Phase II.

Results for energetic materials will be discussed for soil in Jimmy Lake and Shaver River Ranges. For surface water samples, no explosives were detected in any water samples except for the water sample collected in a crater in Shaver River Range. When munitions or debris were encountered, subsamples were collected as near as possible around the UXO.

Alpha Range

Vegetation. The results for the vegetation samples showed that some parameters exceeded the background level value (BGL). Of the 27 parameters analyzed, only 14 (Al, Sb, As, Cd, Ca, Cu, Fe, Pb, Ni, Na, Sn, Ti, V, and Zn) were detected at values higher than the BGL. All of the parameters that exceeded the BGL had concentrations very close to the background values except for Al, Fe, Pb, Na and Ti in one linear transect. Curiously, no parameters exceeded any background values in all other linear transect samples. Results indicated little or no phytoaccumulation of metals in this range.

Surface water. The only surface water sample collected in a small puddle in Alpha Range was highly contaminated by most of the metals. Al, As, Ba, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Tl, V, and Zn were detected at concentrations higher than the CCME criteria. Based on the aluminum value, a low-order detonation of an item containing tritonal may have occurred in that puddle. The metal concentrations were very high, but considering the limited amount of water in the puddle, this represents a small impact to the range.

Bravo Range

Vegetation. Of the 27 parameters analyzed, only Cr, Fe, Pb, Na, Sr, Ti, V, and Zn were detected at values higher than the BGL. However, concentrations were of the same order of magnitude as in Phase I, indicating limited or no accumulation. Some analytes identified as a problem during Phase I, Al, Ba, Cd, and Cu, were not a problem during Phase II. The difference is probably due to the soil removed during cleaning of the sites, which decreased the concentrations by mixing surface soil with cleaner deeper soil. Nevertheless, as in Phase I, this site was considered not contaminated.

Jimmy Lake Range

Soils. Some parameters exceeded the background level values. Of the 20 parameters analyzed, Cd, Cr, Cu, Pb, Ni, V, and Zn were detected at values higher than the BGL or the ASQGL, and in some occasions were higher than the Industrial Soil Criteria in the bombing circle area. The strafing area showed only copper at values higher than the BGL, especially in front of the targets, showing that our approach was efficient for characterizing the surface. The strafing area was not contaminated compared to the bombing circle area, where all the samples showed concentrations higher than the BGL, the ASQG, or the IndSQG for many parameters. Compared to Phase I, the same analytes were problematic, with cadmium concentrations exceeding the ASQG in all of the samples. High cadmium concentrations can come from the rocket paints that may contain this metal as an anti-corrosive or as part of the internal parts of the warheads. The most probable hypothesis is that cadmium is part of the painting of the rockets, since a problem had already been encountered in the warehouse where they were cleaning the launchers. If recovered from the cleaning of the launchers, cadmium vaporization resulting from the intense heat during the firing of the rockets is likely responsible for the deposition of this metal in the launcher. This was supported by a recent paper by Boggs (2004), who mentioned that cadmium, zinc, and chromium are important metal components of bomb paints that are released into the environment during open detonation. On impact with the ground or with the target, debris of rockets may deposit cadmium on the ground, which would explain the high concentrations of this metal at this site. Chromium concentrations exceeded the BGL for many, but not all, of the samples. Copper was observed at concentrations higher than the IndSQG in six bombing circle samples, while 14 samples exceeded the ASQG and the other was higher than the BGL. All of the samples of the bombing area exceeded the BGL for Pb, Ni, V, and Zn. The concentrations in the bombing area of Jimmy Lake Range are of the same magnitude as during Phase I. The impacts of training activities on Jimmy Lake Range are clearly important. Only copper exceeded the IndSQG; therefore, particular attention should be given to this parameter and to cadmium as well. Legally, since the site use will not change, i.e., it will continue to be a target area, no action is required; however, to demonstrate due diligence, a thorough cleaning of the small surface area should be conducted, and the soils should be removed and sent to a secure landfill, especially if the hydrogeology study demonstrates that cadmium or copper are problematic in groundwater.

Vegetation. Only one vegetation sample was collected in the bombing area, while 15 samples were collected in the strafing area. For the sample in the bombing area, of the 27 parameters analyzed, Ca, Cu, Fe, Pb, Se, Na, and V exceeded the BGL. Most of the parameters that exceeded the BGL in vegetation samples also exceeded the BGL in soil, except for Ca, Na, and Se. Surprisingly, cadmium did not exceed the BGL in vegetation. This can be explained by the fact that different metals may have different extractability and some metals are preferentially extracted from the soils by the plants.

Energetic Materials. On Jimmy Lake Range, almost all samples collected in the bombing area contained the propellant-related compound nitroglycerine (NG) deposited around the target at concentrations varying from 170 to 3,590 ppb. TNT was detected at 70 ppb in only one sample. Compared to the results

obtained during Phase I, the situation is similar, but the concentrations of nitroglycerine are higher. Also, during Phase I, TNT was found in almost all samples collected in the bombing area; this was not observed in Phase II. The nitroglycerine source is double- or triple-based propellants that were spread on site by incompletely burned rockets. Since the concentrations of explosives were quite low, no action is required to correct the situation with explosives at this site.

Shaver River Range

Soils. Of the 20 parameters analyzed, only Cd, Cu, and Pb were detected at values higher than the BGL or the ASQGL. Cadmium is again problematic at concentrations higher than the ASQG for most of the samples collected with the circular strategy. Even if most of the cadmium concentrations are higher than the ASQG, the levels are lower than in the Jimmy Lake bombing area. The effects of the activity conducted in the Shaver River Range are different from those in the Jimmy Lake Range. Copper and lead concentrations were higher than the BGL, but not all samples showed elevated concentrations. Curiously, soil collected in the crater 2–3 m away from the target showed no concentrations higher than background levels. This shows that the metal concentrations are very localized around the target. Compared with the results from Phase I, the situation is almost identical, except that antimony, which had been problematic during Phase I, did not exceed the IndSQG during Phase II.

Surface Water. The only surface water sample collected in a crater was highly contaminated with most of the metals. Al, Cd, Cu, Fe, Pb, Mn, and Zn were detected at concentrations much higher than the CCME criteria. The high aluminum value suggests that a low-order detonation of an item containing tritonal took place in that crater. The elements of concern in this crater are almost identical to the one encountered in the small puddle in Alpha Range. The same conclusion can be drawn here; the metal concentrations were very high, but considering the limited amount of water in the crater, this represents a small impact to the range.

Energetic Materials. All of the soil samples collected at the Shaver River Range were analyzed for energetic materials. No explosives were found in the three background samples. No propellant residues were found in any circular samples, but some were found in the surface water sample collected in the crater. The NG concentration was 2 ppb, while 1,3-DNB, 2,6-DNT, and 2,4-DNT concentrations were, respectively, 595, 377 and 6,486 ppb. In the soil samples collected in the crater, TNT was found at 79.38 ppm, while it was found at 13.10 ppm in the water collected in the crater. RDX was not found in the soils of the crater but was found at 2 ppm in the surface water sample collected in that crater. High concentrations of TNT in the soils and water in the crater could indicate a recent low-order detonation during a blow-in-place operation using a C-4 block. 1,3,5-TNB was also detected at 350 ppb in the soils of the crater. while it was not detected in the water sample. 1,3,5-TNB can be found as a propellant impurity, but it can also occur as a TNT impurity or a TNT photolysis product. In this case, TNB probably comes from the photolytic decarboxylation of TNT.

TNT was found in all soil samples collected in Shaver River Range. The TNT concentrations for the soil samples collected in a circular pattern around the target were much higher than for other soil samples. Concentrations above 50 ppm were found in samples from the A, B, and C rings, with the highest concentration at 165 ppm (compared to 332 ppm during Phase I). Here again, much lower concentrations of TNT-related compounds, such as 2.4-DNT, 2.6-DNT, 1,3,5-TNB, 2-ADNT, and 4-ADNT, were found in the samples. As an example, 1,3,5-TNB was found at concentrations of 0.23-1.66 ppm in 22 out of 32 soil samples from the circular sampling strategy. In two samples from the target area, very low concentrations of RDX (350 and 6000 ppb) and HMX (1470 ppb) were found. Neither RDX nor HMX were detected in the samples that contained the highest concentrations of TNT. Thus the source of these small amounts of RDX found on the Shaver River Range appears to be different from the source of the TNT. The source of TNT at this range is thought to be the tritonal used as the high explosive in Air Force bombs. Tetryl was not detected in any samples. Compared to results obtained during Phase I, the situation is very similar, with small differences such as no tetryl and a higher TNT maximum concentration during Phase I. In general, in Shaver River Range the concentrations of explosives (mainly TNT) were much higher than in the other ranges. Most of the TNTrelated compounds were found in almost all the samples. RDX and HMX were found at very low concentrations. TNT was the most important contaminant.

In front of the target in this range, 100 discrete minigrid samples and 4 composites of 30 subsamples were collected from a 10- × 10-m grid. Six explosives-related compounds were detected in all of these samples, with TNT being present at a factor of 11 or greater than any of the other compounds. The other compounds detected were either manufacturing impurities in military-grade TNT (2,4-DNT) or environmental transformation products of TNT (1,3,5-TNB, 1,3-DNA, 2-ADNT, 4-ADNT).

The grand mean concentration of TNT was 10.7 mg/kg (the relative standard deviation was 5.55 percent) in these four replicate samples. The mean concentrations for the other analytes detected in these composite samples (in the order of decreasing concentrations in mg/kg) were 2-ADNT (1.19), 4-ADNT (0.776), 3,5-DNA (0.263), 1,3,5-TNB (0.107), and 2,4-DNT (0.098). The relative standard deviations for these compounds ranged from 5.83 percent to 9.20 percent. Thus, very repeatable sampling was achieved for this 10- × 10-m grid area using 30-increment composite samples, even with respect to the minor components present at low concentrations. Each of the four 30-increment samples was analyzed in triplicate. Subsampling error for each of the four replicates was estimated by pooling the relative standard deviations for the six compounds. These pooled percent RSDs ranged from 2.95 to 5.93 percent, indicating that the method used to process these samples was effective at minimizing subsampling error for these large composite samples weighing about a kilogram.

The same six compounds detected in the 30-increment composite samples from this area were also detected in almost all of the discrete samples, although the concentrations varied by as much as three orders of magnitude. RDX and HMX were also detected in 19 and 4 of these discrete samples, respectively, but were not detected in any of the four 30-increment composite samples.

TNT concentrations varied from 0.381 to 289 mg/kg in these discrete samples, a range of nearly three orders of magnitude, with a mean value of 16.2 mg/kg. Clearly, the use of a single discrete sample or even several discrete samples to estimate the mean concentrations in this 10- × 10-m area would be prone to large sampling error. The highest RDX concentration was 35.4 mg/kg in minigrid # 42, but the TNT in this sample was only 0.657 mg/kg, indicating that the source of the RDX was probably not the same source that led to widespread TNT concentrations within the overall 10- × 10-m grid. The source of the RDX is uncertain but could have been C4 used as a donor charge to detonate dudded bombs on this range. The fact that none of the other minigrids surrounding minigrid # 42 had RDX concentrations in excess of 0.179 mg/kg indicates that a small piece of RDX-based explosive may have been present in the discrete sample collected from minigrid #42.

The distribution of TNT values for these 100 minigrid samples is shown in Figure 5-4 as a histogram with a bin size of 5 mg/kg. Clearly, this distribution is non-Gaussian, as has been found elsewhere for energetic compounds at other types of training ranges (Jenkins 2004, in press). Sixty-eight of the discrete samples had TNT concentrations that were less than the mean of 16.2 mg/kg. The concentration of TNT versus position within the $10-\times10$ -m grid is presented in Figure 5-5. Upon close inspection, one set of higher concentrations of TNT might be present in a line from minigrid #41 (which had the highest TNT concentration of 289 mg/kg) diagonally to minigrid # 5, although other minigrids randomly located within the overall $10-\times10$ -m grid had similar concentrations. No clear-cut hot spots of high concentrations were distinguishable.

While we collected four 30-increment composite samples within this 10- × 10-m area, multi-increment composites with various numbers of increments from the 100 discrete samples can be mathematically simulated. This is valid because multi-increment composite samples are a physical average of the increments used to create the composite, and equivalent results have been shown if the increments are individually analyzed and combined mathematically or composited and the composite subsampled and analyzed (Jenkins et al. 1997a).

Sets of 50 multi-increment results for TNT were simulated from the 100 discrete samples for values of n ranging from 5 to 50. A random number generator was used to select values with replacement. The minimum, maximum, mean, median, standard deviation, and tolerance limits (5 percent) for these distributions are shown in the DRDC Report. Histograms for the distributions for n equal to 5, 30, and 50 were done and, as expected, as the number of increments per sample increases, the difference between the minimum and maximum decreases and the median and mean come closer together. The trend toward a more Gaussian distribution (as predicted from the central limit theorem of statistics) is less observable in these data than for similar data sets from other sites with residues of energetic compounds (Jenkins et al. 2004). The presence of several high concentrations for individual minigrid samples, such as minigrid #41, where the TNT concentration was 289 mg/kg, and minigrid # 37, where the TNT concentration was 100 mg/kg, may account for this observation or relationship. Nevertheless, increasing the number of increments per composite sample does reduce the tolerance range or improve the likelihood of obtaining a result that is an acceptable estimate of the mean. Thus, the recommendation based on the statistical analysis is that the best representative sample for the area is a multiincrement sample and not one or several discrete samples. At least 30–50 subsamples were demonstrated as necessary to achieve a representative sample.

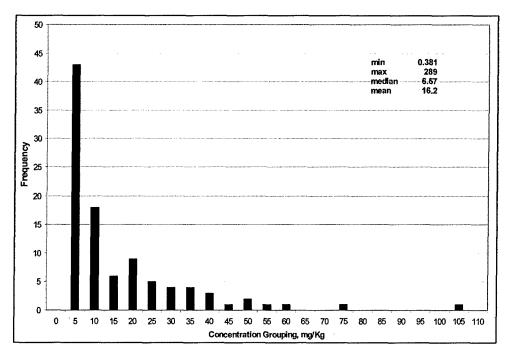


Figure 5-4. Distribution of TNT concentrations at Shaver River Range

Primrose Lake, Jimmy Lake, and the Shaver River

Sediments. Some metals parameters exceeded the ISQG or the Probable Effect Level (PEL). Only two parameters exceeded the CCME threshold criteria: As and Hg. For As, only two samples in Jimmy Lake and four samples in Primrose Lake exceeded the most severe IndSQG but were of the same order of magnitude. For mercury, only three samples, all in Jimmy Lake, exceeded the IndSQG. One even exceeded the most permissive PEL criterion. All of the other parameter concentrations were below the CCME IndSQG or CCME PEL criteria, showing that the sediments are not contaminated.

Surface water. Of the 30 parameters measured in surface water samples, only Al, Cu, Fe, and Ag exceeded the CCME threshold criteria. For aluminum, all samples showed concentrations within the interval of the CCME criterion. High levels of aluminum and arsenic are not unusual in western water bodies. This had already been observed in CFB Shilo, where aluminum, arsenic, and iron were naturally elevated (Ampleman et al. 2003). A cadmium concentration at 0.3 ppb was observed in one sample. Copper concentrations in surface water samples in Jimmy Lake were within the interval of the CCME criterion, while in the sample collected in Shaver River, the copper concentration was twice the CCME criterion. Iron was also observed in the Shaver River sample at three times the CCME criterion. Concentrations of all the other parameters were lower than the CCME criteria, except for one sample in Jimmy Lake, where silver was detected at five times the CCME criterion. During Phase I, silver was also detected in Jimmy Lake. We have no explanation for this anomaly. No other

samples in Jimmy Lake demonstrated the presence of silver. No explosives were detected in any of the surface water samples. No explosives were detected in the surface water sample collected at the mouth of the Shaver River. In general, water in both lakes can be considered uncontaminated.

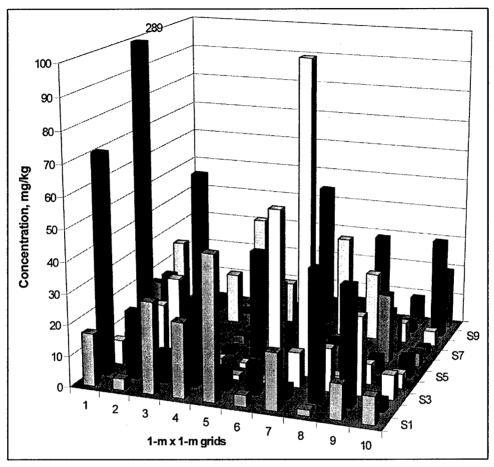


Figure 5-5. Position of TNT concentrations at Shaver River Range

Remote areas

Soils. Of the 20 parameters analyzed, only Co, Cu, Pb, Sr, and V were detected at values higher than the BGL in some samples collected in remote areas. No parameters were detected at values higher than the ASQG or the IndSQG. Samples collected in site C-284, where the old oilrigs were located, showed concentrations higher than the BGL, but these concentrations were nevertheless low. The quality of the soils in the remote areas is comparable to background, showing that the activities have a limited effect on these environments. No action is required on these sites.

Vegetation. Of the 27 parameters analyzed, only Al, As, Ba, Cd, Fe, Pb, Mn, and Zn exceeded the BGL. The metals that exceeded the BGL in vegetation samples were not the same as the ones that exceeded the BGL in soils. Nevertheless, the accumulation of these metals was not extensive. Most of the

concentrations were very close to the BGL, indicating that the vegetation is not very contaminated.

Surface water. Nine surface water samples including two duplicates were collected. Out of the 30 metals measured in surface water samples, Al, Cd, Cu, Fe, Mn, Se, and Zn exceeded the CCME threshold criteria. For aluminum, most of the samples showed concentrations higher than the interval of the CCME criterion. High levels of aluminum and arsenic are not unusual in western water bodies, as previously mentioned. Cadmium concentrations were observed in three water samples mainly in C-295, the first site visited. Copper and iron were found at high concentrations in almost all samples; however, only one or two samples showed concentrations higher than the CCME criteria for Mn, Se, and Zn.

Global results in all ranges

Generally, the concentrations of metals in soils in all of the ranges were close to the BGL concentrations and below the ASQG or the IndSQG. However, some metals were systematically present at high concentrations, such as cadmium, copper and zinc, and can be related to firing activities. Compared to results obtained during Phase I, fewer metals exceeded the IndSQG in Phase II. Examples of exceedances include antimony in Shaver River Range and cadmium in Jimmy Lake Range. The fact that metals concentrations were low in the ranges is the direct result of good management of the sites performed at Cold Lake. During both visits in August 2002 and 2003, the sites were clean of debris and large pieces of metal. Furthermore, often when we arrived on site, the ranges had been freshly tilled. In spite of regular tilling of the sites, the results from Phase I and Phase II are comparable, revealing the same tendencies in the two consecutive years. In general, the removal of metals, which is performed on a regular basis, is an excellent practice and makes a significant contribution to environmental stewardship.

When the ranges are compared, the conclusions drawn from Phase I results are still valid for Phase II. Jimmy Lake Range is still the site most contaminated by metals; Bravo Range is less contaminated than Alpha Range; and Shaver River Range is also less contaminated than Alpha Range. In Shaver River Range, fewer metals were detected compared to Alpha Range, but the concentrations were of the same order of magnitude. The metals in Shaver River Range that had high concentrations and were of concern, such as cadmium, are similar to the metals of concern encountered in Jimmy Lake Range but at lower concentrations. Problematic metals seem to be found in different types of weapons. For example, cadmium is not only part of the rocket painting, but if can also be part of bomb painting, as pointed out by Boggs (2004).

The vegetation analyses revealed that some metals are phytoaccumulated from the soils, since direct relations between soil and vegetation metal concentrations were identified in almost all of the ranges. The metals in plants did not always correspond to the metals with high concentrations in soils. Furthermore, not all of the metals were phytoaccumulated, which may be the result of selective adsorption. Considering the results obtained during Phase II, the quality of the

vegetation is excellent and compares well with the concentrations of the background samples. Therefore, vegetation does not represent a risk to wildlife.

Surface water and sediments were sampled during Phase II, and the results indicated that these sediments were not contaminated, with only a few exceptions. Surface water sample results also revealed that the concentrations of metals were quite low, and no explosives were found. In general, neither the sediments nor the surface water was contaminated in Primrose Lake and in Jimmy Lake.

For the energetic materials analyses, our efforts were concentrated mainly on Jimmy Lake and Shaver River Ranges during Phase II, since explosive concentrations determined in Alpha and Bravo Ranges during Phase I revealed low ppm levels. In Jimmy Lake Range, in the circular samples, mainly propellant residue was found, such as nitroglycerine, which was found in all samples. This indicates that rockets are often used at this site. In Shaver River Range, the situation was the opposite; very little propellant residue was found, but explosives such as TNT were found in almost all samples. This indicates that mainly bombs are used at this site. The metals that showed problems in Shave River Range are the same as in Jimmy Lake Range but at lower concentrations. Little information about weapon compositions is available that can explain all of these results. The most probable explanation is that the problem metals are found in both rocket and bomb paints. The maximum TNT concentration obtained during Phase II was lower than the concentration obtained during Phase I. This can be the result of site tilling.

In general, except in Jimmy Lake Range, the soil, the vegetation, the surface water, and the sediments are of excellent quality. No action is required on any site except to continue to clean and manage the sites as currently. Metal concentrations in the bombing area of Jimmy Lake Range are especially high. Although most of them did not exceed the ISQG criteria, many of the results are higher than the ASQG. As already mentioned, legally, no action is required, since the site will not be used for agriculture but will continue to be used for target practice. The most important results will come from the hydrogeological study. Nevertheless, to exercise due diligence, removing soil from the bombing area and send it to a secure landfill will solve this problem for a very long time.

Summary and Conclusions

In August 2002 DRDC-Valcartier and CRREL conducted Phase I to characterize the soil, vegetation, and surface water for metals and energetic materials. A total of 193 soil, 16 vegetation, and 4 surface water samples were collected during Phase I in Alpha, Bravo, Jimmy Lake, Shaver River, and open detonation and rifle ranges. A few surface water samples were collected in Primrose Lake, Jimmy Lake, the Shaver River, and a pond containing ammunition in Shaver River Range. In August 2003, DRDC-Valcartier and CRREL conducted Phase II of the study to complete the characterization of the soil, vegetation, surface water, and sediment for metals and energetic materials. A total of 324 soil, 69 vegetation, 19 surface water, and 28 sediment samples were collected during

Phase II. Efforts were mainly in Jimmy Lake and Shaver River Ranges and also in Primrose Lake and Jimmy Lake.

Two strategies were used to collect samples across the ranges. The first consisted of using a linear sampling pattern. This approach was used during Phase I to evaluate whether the level of contamination by metals was following a pattern with distance from the target. The same approach was used in Alpha Range to collect vegetation samples and in Jimmy Lake Range, where we modified the strategy by fixing the 40 percent transect at the target position. The concentrations behind and in front of the target were then determined. This proved to be an adequate approach, since the results showed that metals accumulated mainly in front of the targets. The second sampling strategy was the circular approach, also developed during Phase I and applied to targets in the Jimmy Lake and Shaver River Ranges. The strategy consisted of compositing samples taken in a circular pattern around targets. Twenty-six soil samples were collected, one within each of the cells around the target. Furthermore, in Shaver River Range, one hundred 1- × 1-m minigrids were constructed, and 100 discrete samples were collected to evaluate the dispersion and the heterogeneity of the explosives in front of the tank. This statistical evaluation revealed again the great heterogeneity encountered with explosive contamination and emphasized that compositing with 30 increments is the best approach to collecting soils for explosive analysis. In all other ranges such as in the remote areas, simple composite sampling was done around targets or existing infrastructures used as targets.

Generally, as observed during Phase I, results from Phase II showed that the concentrations of metals in soils in all of the ranges were quite low. Most of the time, the metals detected at concentrations higher than the BGL were no greater than twice the BGL value and far below the ASQGL, except for some metals such as cadmium, copper and zinc, which were present at higher concentrations. These metals can be related to firing activities. Nevertheless, most of the values were quite low. Only copper in Jimmy Lake Range exceeded the ISQG. The fact that metals concentrations were low is the direct result of good management of the sites. During our visit, the sites were clean and no debris or large pieces of metals were observed. Debris is controlled by removing the pieces of metals on a regular basis and tilling the soil often. Results from Phase I and Phase II are comparable in two consecutive years.

When the ranges are compared, the conclusions drawn from Phase I results still apply: the Jimmy Lake Range is the most contaminated site by metals; Bravo Range is less contaminated than Alpha Range; and Shaver River Range is also less contaminated than Alpha Range. In Shaver River Range, fewer metals were detected compared to Alpha Range, but the concentrations were of the same order of magnitude. The metals in Shaver River Range that had high concentrations and were of concern, such as cadmium, were similar to the metals of concern encountered in Jimmy Lake but at lower concentrations. Problematic metals seem to be found in different types of weapons such as bombs and rockets and are likely part of their paints. Little information about weapon compositions is available that can explain all of these results, but the most probable explanation is that the problem metals are found in both rocket and bomb paints.

The vegetation analyses revealed that some metals are phytoaccumulated from the soils, since a direct relation between soil and vegetation concentrations was identified. On some occasions, metals phytoaccumulation did not correspond to the metals concentrations in soils. Not all of the metals were phytoaccumulated, possibly due to selective adsorption. Nevertheless, considering the results obtained during Phase II, the quality of the vegetation compared well with the concentrations in background samples and does not represent a risk to wildlife.

Surface water and sediment were sampled during Phase II to assess the quality of Primrose Lake and Jimmy Lake. Many sediment samples were collected in both lakes using a manual grabber. Analyses of the surface water samples revealed that the concentrations of metals were quite low, and no explosives were found. In general, neither the sediment nor the surface water is contaminated in Primrose Lake and Jimmy Lake.

For the energetic materials analyses, our efforts concentrated mainly on Jimmy Lake and Shaver River Ranges during Phase II, since explosive concentrations determined in Alpha and Bravo Ranges during Phase I revealed low ppm levels. In Jimmy Lake, in the circular samples, mainly propellant residues were found, such as nitroglycerine, which was found in all samples. This indicates that rockets are often used at this site. The concentrations of explosives were low and do not represent a major problem. In Shaver River Range, the situation was the opposite; very little propellant residues were found, but explosives such as TNT were found in almost all samples. This indicates that bombs are mainly used at this site. The maximum TNT concentration obtained during Phase II was lower than the concentration obtained during Phase I. This can be the result of site tilling.

In conclusion, this study demonstrated that the ranges have some accumulation of metals due to firing activities, but the extent of contamination does not reach levels of concern. Contamination by explosives is also minimal except in Shaver River Range, where TNT was found at high concentrations (ppm level). In general, except for Jimmy Lake Range for the metals and in Shaver River Range for the energetics, the soil, the vegetation, the surface water, and the sediment are of excellent quality. No action is required on any site except to continue to clean and manage the sites the way it is currently done. Metal concentrations in Jimmy Lake Range in the bombing area are especially high. Although most of them did not exceed the ISQG criteria, many of the results are higher than the ASQG. As already mentioned, legally, no action is required, since the site will not be used for agriculture but will continue to be used for target practice. The most important results will come from the hydrogeological study. Nevertheless, to exercise due diligence, removing soil from the bombing area and sending it to a secure landfill will solve this problem for a very long time.

Finally, it was observed that the Air Force base environmental situation is different from the Army bases in the sense that in Army bases, a bigger amount of smaller weapons are fired on a daily basis, compared to rockets launching and bomb dropping in air bases. This leads to a more important accumulation and dispersion of the metallic debris in Army bases, but the concentrations of explosives are in general lower, considering that smaller weapons lead to smaller dispersion of energetics, especially during blow-in-place operation and low-order

detonations. The Army anti-tank ranges are the only exception, since the M-72 weapons have a high dud rate and lead to high concentrations of explosives in the soil. Another difference resides in the fact that the Army uses more Composition B and Octol than the Air Force, which uses mostly tritonal as explosive. Nitramine explosives are known to give better detonation and combustion when high-order detonation is occurring, leading to lower concentrations of explosives. Furthermore, larger bombs dropped by air leads to less- dispersed metallic debris; this, combined with the good practice of removing often this large debris, results in a better contribution to environmental stewardship.

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6 Update on Massachusetts Military Reservation

Introduction

During the period of 1 October 2003 through 30 September 2004, environmental investigations continued at Camp Edwards, located on the northern portion of the Massachusetts Military Reservation (MMR) near Falmouth, MA (USA) on Cape Cod. The Training Ranges and Impact Area at Camp Edwards encompass approximately 14,000 acres. The approximately 2,200-acre Impact Area contains artillery and mortar targets used for training activities since 1908. The highest frequency of use occurred during and after World War II. Surrounding the Impact Area are numerous firing ranges, artillery and mortar positions, and training areas. Firing of high-explosive (HE) artillery rounds was discontinued in 1989. Low-intensity training rounds (LITR) and inert and HE mortar rounds were fired until 1997, when a moratorium on artillery and mortar firing was established by the U.S. Environmental Protection Agency (EPA). A comprehensive site assessment has been underway since 1997. Site investigations have addressed a variety of training activities associated with firing ranges (rocket or anti-tank, artillery, mortar, and small arms), open burn/open detonation (OB/OD) sites, and firing positions.

Over 40 summary reports and work plans have been prepared over the last year covering the activities at Camp Edwards (Appendix A). In addition, three papers have been published and another is in review (Morley et al., in prep.), as well as 12 papers presented at conferences. Three significant reports are in the process of development: a Central Impact Area Soil Report, a Central Impact Area Groundwater Feasibility Study Report, and a Surface to Groundwater Link Report.

Site overview

Soils at the site consist of fine to coarse-grained sands overlying very coarse sands and gravels residing at the top of the saturated zone. Silt and clay comprise the base of the saturated zone, which overlies relatively impermeable bedrock located at a depth of 285–365 ft below ground surface (bgs). Depth-to-water over most of the site is approximately 100 ft. The Camp Edwards Training Ranges and Impact Area lie directly over the Sagamore Lens, a major groundwater recharge

area and the most productive portion of the Cape Cod Aquifer. The apex of the Sagamore Lens is located at the southeast corner of the Impact Area, from which groundwater flows radially in all directions. The ocean bounds the aquifer on three sides. Except on extreme slopes, surface water runoff at Camp Edwards is virtually nonexistent because of the highly permeable nature of the soils and aquifer material.

Since the last update (Pennington et al. 2003), several thousand soil and groundwater samples have been collected at Camp Edwards (Table 6-1). Table 6-1 lists the number of samples by media and site collected from 1 October 2003 to 30 August 2004. This past year's effort has focused on the Impact Area, Southeast (SE) Ranges, and the Northwest Corner.

Table 6-1 Location, Media, and Number of Environmental Samples Collected at Camp Edwards from 1 October 2003 to 30 August 2004

	Impact Area	Demo 1	Demo 2	SE Ranges	Phase IIB Sites	Bourne	NW Corner	Other	Total
Surface Soil (0-2 ft)	89	2	6	573	39	11	133	386	1232
Deep Soil > 2 ft	130	0	0	11	0	0	4	0	145
GW Well	482	187	6	559	0	957	130	773	3094
GW Profile	0	15	13	121	0	69	194	0	412

Demo 1 - Demolition Area 1

Demo 2 - Demolition Area 2

GW - Groundwater

NW Corner - Northwest Corner

The data from these studies are summarized for soil and groundwater in Tables 6-2 and 6-3, respectively. No new explosive compounds have been detected since the last update. Figure 6-1 is the distribution of munition explosive constituents (MEC) observed in surface soil (0–2 ft) at Camp Edwards. The largest proportion of MEC observed are the amino-dinitrotoluenes (aDNTs) and dinitrotoluenes (DNTs), followed by 2,4,6-trinitrotoluene (TNT), the "Other" category, perchlorate, hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) in decreasing order of frequency. The "Other" category includes di-n-butyl phthalate, di-n-octyl-phthalate, N-nitrosodiphenylamine, and polychlorinated napthalenes (PCNs). Di-n-butyl phthalate and N-nitrosodiphenylamine (an oxidation product of diphenylamine) are propellant compounds, whereas PCN is present in some HalowaxTM fillers used to simulate the mass of HE. The overall distribution of MEC is similar to past years, with a slightly higher frequency of the aDNTs. Unlike last year, no white phosphorus was detected in any soil samples.

Table 6-2 Summary of Camp Edwards Validated Soil Data from 1 October 2003 through 30 August 2004

Analyte	Units	# Detects	# Samples	Min.	Max.	Mean
1-(METHYLAMINO) - ANTHRAQUINONE	µg/kg	10	10	ND	ND	IND
1,1,1-TRICHLOROETHANE	µg/kg	0	58	ND	ND	ND
1,1,2,2-TETRACHLOROETHANE	µg/kg	0	58	ND	ND	ND
1.1.2-TRICHLOROETHANE	µg/kg	0	58	ND	ND	ND
1,1-DICHLOROETHANE	µg/kg	0	58	ND	ND	ND
1,1-DICHLOROETHENE	µg/kg	0	58	ND	ND	ND
1,2,3,4,6,7,8-HEPTACHLORODIBENZOFURAN	pg/g	14	15	0.92	47.00	5.82
1,2,3,4,6,7,8-HEPTACHLORODIBENZO-P-DIOXI	pg/g	15	15	5.60	36.00	18.59
1,2,3,4,7,8,9-HEPTACHLORODIBENZOFURAN	pg/g	1	15	0.49	0.49	0.49
1,2,3,4,7,8-HEXACHLORODIBENZOFURAN	pg/g	10	15	0.44	0.84	0.62
1,2,3,4,7,8-HEXACHLORODIBENZO-P-DIOXIN	pg/g	2	15	0.26	0.30	0.28
1,2,3,6,7,8-HEXACHLORODIBENZOFURAN	pg/g	12	15	0.24	1.60	0.71
1,2,3,6,7,8-HEXACHLORODIBENZO-P-DIOXIN	pg/g	2	15	0.68	0.86	0.77
1,2,3,7,8,9-HEXACHLORODIBENZOFURAN	pg/g	0	15	ND	ND	ND
1,2,3,7,8,9-HEXACHLORODIBENZO-P-DIOXIN	pg/g	3	15	0.44	0.67	0.54
1,2,3,7,8-PENTACHLORODIBENZOFURAN	pg/g	6	15	0.44	0.64	0.44
1,2,3,7,8-PENTACHLORODIBENZO-P-DIOXIN	pg/g	0	15	ND	ND	ND
1,2,4-TRICHLOROBENZENE	µg/kg	0	350	ND	ND	ND
1,2-DIBROMO-3-CHLOROPROPANE		0	21	ND	ND	ND
1,2-DIBROMO-3-CHLOROFROFANE 1,2-DIBROMOETHANE (ETHYLENE DIBROMIDE)	µg/kg µg/kg	0	43	ND	ND	ND
1,2-DICHLOROBENZENE		0	350	ND	ND	ND
1,2-DICHLOROBENZENE	μg/kg	0	58	ND	ND	ND
1,2-DICHLOROPROPANE	μg/kg μg/kg	0	58	ND	ND	ND
1,3,5-TRINITROBENZENE	µg/kg	1	711	120.00	120.00	120.00
1,3-DICHLOROBENZENE	µg/kg	0	350	ND	ND	ND
1,3-DIETHYL-1,3-DIPHENYL UREA	µg/kg	3	329	38.00	530.00	349.33
1,3-DINITROBENZENE	µg/kg	0	711	ND	ND	ND
1,4-BIS (P-TOLUIDINO) ANTHRAQUINONE	µg/kg	0	10	ND	ND	ND
1,4-DIAMINO-2,3-DIHYDROANTHRAQUINONE	µg/kg	0	10	ND	ND	ND
1,4-DICHLOROBENZENE	µg/kg	0	350	ND	ND	ND
2,2'-OXYBIS(1-CHLORO)PROPANE	μg/kg	0	329	ND	ND	ND
2,3,4,6,7,8-HEXACHLORODIBENZOFURAN	pg/g	11	15	0.34	0.92	0.59
2,3,4,7,8-PENTACHLORODIBENZOFURAN	pg/g	9	15	0.55	1.20	0.83
2,3,7,8-TETRACHLORODIBENZOFURAN	pg/g	12	15	0.29	1.20	0.72
2,3,7,8-TETRACHLORODIBENZO-P-DIOXIN	pg/g	0	15	ND	ND	ND
2,4 DB	µg/kg	0	27	ND	ND	ND
2,4,5-T (TRICHLOROPHENOXYACETIC ACID)	µg/kg	0	27	ND	ND	ND
2,4,5-TRICHLOROPHENOL	μg/kg	0	329	ND	ND	ND
2,4,6-TRICHLOROPHENOL	µg/kg	0	329	ND	ND	ND
2,4,6-TRINITROTOLUENE	μg/kg	39	711	14.00	3300000	119279.97
2,4-D (DICHLOROPHENOXYACETIC ACID)	μg/kg	0	27	ND	ND	ND
2,4-DIAMINO-6-NITROTOLUENE	μg/kg	0	710	ND	ND	ND
2,4-DICHLOROPHENOL	μg/kg	0	329	ND	ND	ND
2,4-DIMETHYLPHENOL	μg/kg	0	329	ND	ND	ND
2,4-DINITROPHENOL	μg/kg	0	329	ND	ND	ND
2,4-DINITROTOLUENE	μg/kg	31	1040	14.00	54000.00	3142.42
2,6-DIAMINO-4-NITROTOLUENE	μg/kg	0	711	ND	ND	ND
2,6-DINITROTOLUENE	μg/kg	6	1040	14.00	29.00	20.83
2-AMINO-4,6-DINITROTOLUENE	μg/kg	62	711	14.00	9200.00	409.31
2-CHLOROBENZALDEHYDE	μg/kg	0	329	ND	ND	ND
						(Continued)

Table 6-2 (Continued)						
Analyte	Units	# Detects	# Samples	Min.	Max.	Mean
2-CHLOROBENZOIC ACID	μg/kg	0	323	ND	ND	ND
2-CHLOROETHYL VINYL ETHER	µg/kg	0	21	ND	ND	ND
2-CHLORONAPHTHALENE	μg/kg	0	329	ND	ND	ND
2-CHLOROPHENOL	μg/kg	0	329	ND	ND	ND
2-HEXANONE	µg/kg	0	58	ND	ND	ND
2-METHYL-3-NITROANILINE	μg/kg	0	329	ND	ND	ND
2-METHYL-5-NITROANILINE	µg/kg	0	329	ND	ND	ND
2-METHYLNAPHTHALENE	µg/kg	1	329	23.00	23.00	23.00
2-METHYLPHENOL (O-CRESOL)	μg/kg	0	329	ND	ND	ND
2-NITROANILINE	μg/kg	0	329	ND	ND	ND
2-NITRODIPHENYLAMINE	µg/kg	0	329	ND	ND	ND
2-NITROPHENOL	μg/kg	0	329	ND	ND	ND
2-NITROTOLUENE	µg/kg	1	711	71.00	71.00	71.00
3,3'-DICHLOROBENZIDINE	μg/kg	0	326	ND	ND	ND
3,5-DICHLOROBENZOIC ACID	µg/kg	0	27	ND	ND	ND
3.5-DINITROANILINE	μg/kg	0	329	ND	ND	ND
3-CHLOROBENZALDEHYDE	μg/kg	0	329	ND	ND	ND
3-NITROANILINE	µg/kg	0 -	329	ND	ND	ND
3-NITROTOLUENE	µg/kg	1	711	58.00	58.00	58.00
4,6-DINITRO-2-METHYLPHENOL	µg/kg	0	329	ND	ND	ND
4-AMINO-2,6-DINITROTOLUENE	μg/kg	62	711	16.00	6600.00	284.40
4-BROMOPHENYL PHENYL ETHER	μg/kg	0	329	ND	ND	ND
4-CHLORO-3-METHYLPHENOL	μg/kg	0	329	ND	ND	ND
4-CHLOROANILINE	μg/kg	0	328	ND	ND	ND
4-CHLOROBENZALDEHYDE	µg/kg	0	329	ND	ND	ND
4-CHLOROPHENYL PHENYL ETHER	μg/kg	0	329	ND	ND	ND
4-METHYLPHENOL (P-CRESOL)	μg/kg	0	329	ND	ND	ND
4-NITROANILINE	µg/kg	0	328	ND	ND	ND
4-NITROPHENOL	μg/kg	0	356	ND	ND	ND
4-NITROTOLUENE	µg/kg	1	711	13.00	13.00	13.00
ACENAPHTHENE	μg/kg	0	329	ND	ND	ND
ACENAPHTHYLENE	μg/kg	4	329	22.00	47.00	31.00
ACETONE	μg/kg	42	58	28.00	1100.00	159.31
ACIFLUORFEN	μg/kg	0	27	ND	ND	ND
ALDRIN	μg/kg	0	29	ND	ND	ND
ALPHA BHC (ALPHA HEXACHLOROCYCLOHEXANE)	μg/kg	0	29	ND	ND	ND
ALPHA ENDOSULFAN	μg/kg	0	29	ND	ND	ND
ALPHA-CHLORDANE	μg/kg	0	29	ND	ND	ND
ALUMINUM	mg/kg	380	380	794.00	42300.00	11714.12
ANILINE	μg/kg	0	326	ND	ND	ND
ANTHRACENE	µg/kg	4	329	27.00	43.00	34.25
ANTIMONY	mg/kg	54	380	0.33	2.20	0.92
ARSENIC	mg/kg	367	380	0.91	12.60	4.28
BARIUM	mg/kg	372	380	2.00	73.20	18.62
BENTAZON	µg/kg	0	27	ND	ND	ND
BENZANTHRONE	μg/kg	0	10	ND	ND	ND
BENZENE	µg/kg	0	58	ND	ND	ND
BENZO(A)ANTHRACENE	µg/kg	23	329	19.00	580.00	101.22
BENZO(A)PYRENE	µg/kg	23	329	18.00	350.00	85.22
BENZO(B)FLUORANTHENE	μg/kg	24	329	21.00	740.00	137.63
BENZO(G,H,I)PERYLENE	μg/kg	15	329	18.00	320.00	77.33
BENZO(K)FLUORANTHENE	µg/kg	26	329	20.00	570.00	118.69
						(Continued

Analyte	Units	# Detects	# Samples	Min.	Max.	Mean
BENZOIC ACID		34	329	18.00	3700.00	264.74
BENZYL ALCOHOL	µg/kg	0	329	ND	ND	ND
BENZYL BUTYL PHTHALATE	µg/kg	2	329	81.00	530.00	305.50
BERYLLIUM	µg/kg	338	380	0.08	0.93	0.32
	mg/kg					
BETA BHC (BETA HEXACHLOROCYCLOHEXANE)	μg/kg	0	29	ND	ND	ND
BETA ENDOSULFAN	µg/kg	0	29	ND	ND	ND
BIS(2-CHLOROETHOXY) METHANE	µg/kg	0	329	ND	ND	ND
BIS(2-CHLOROETHYL) ETHER (2-CHLOROETHYL	μg/kg	0	329	ND	ND	ND
BIS(2-ETHYLHEXYL) PHTHALATE	μg/kg	14	329	18.00	6100.00	767.79
BORON	mg/kg	203	364	0.67	14.90	2.69
BROMOCHLOROMETHANE	μg/kg	0	21	ND	ND	ND
BROMODICHLOROMETHANE	µg/kg	0	58	ND	ND	ND
BROMOFORM	µg/kg	0	58	ND	ND	ND
BROMOMETHANE	μg/kg	1	58	3.00	3.00	3.00
CADMIUM	mg/kg	185	380	0.05	25.50	0.79
CALCIUM	mg/kg	340	380	49.30	5190.00	371.00
CARBAZOLE	μg/kg	1	329	19.00	19.00	19.00
CARBON DISULFIDE	μg/kg	1	58	1.00	1.00	1.00
CARBON TETRACHLORIDE	µg/kg	0	58	ND	ND	ND
CHLORAMBEN	μg/kg	0	27	ND	ND	ND
CHLORDANE	μg/kg	0	12	ND	ND	ND
CHLOROBENZENE	µg/kg	0	58	ND	ND	ND
CHLOROETHANE	µg/kg	0	58	ND	ND	ND
CHLOROFORM	µg/kg	3	58	0.90	3.90	2.47
CHLOROMETHANE	µg/kg	1	58	0.70	0.70	0.70
CHROMIUM	mg/kg	143	143	1.70	65.50	14.25
CHROMIUM, TOTAL	mg/kg	216	237	3.50	47.40	14.71
CHRYSENE	µg/kg	37	329	18.00	860.00	102.11
CIS-1,2-DICHLOROETHENE	µg/kg	0	12	ND	ND	ND
CIS-1,2-DICHLOROETHYLENE	μg/kg	0	9	ND	ND	ND
CIS-1,3-DICHLOROPROPENE	µg/kg	0	58	ND	ND	ND
COBALT	mg/kg	376	380	0.41	17.00	3.09
COPPER	mg/kg	325	380	0.91	3210.00	37.41
CYANIDE	mg/kg	15	200	0.51	6.10	2.14
DALAPON	µg/kg	0	27	ND	ND	ND
DCPA (DACTHAL)	µg/kg	0	27	ND	ND	ND
DDD (1,1-BIS(CHLOROPHENYL)-2,2-DICHLOROE	μg/kg	0	29	ND	ND	ND
DDE (1,1-BIS(CHLOROPHENYL)-2,2-DICHLOROE	µg/kg	11	29	2.50	14.00	7.24
ODT (1,1-BIS(CHLOROPHENYL)-2,2,2-TRICHLO	μg/kg	13	29	2.20	38.00	16.38
DELTA BHC (DELTA HEXACHLOROCYCLOHEXANE)	µg/kg	0	29	ND	ND	ND
DIBENZ(A,H)ANTHRACENE	μg/kg	4	329	18.00	130.00	62.25
DIBENZOFURAN	µg/kg	0	329	ND	ND	ND
DIBROMOCHLOROMETHANE	µg/kg	0	58	ND	ND	ND
DIBROMOMETHANE	µg/kg	0	21	ND	ND	ND
DICAMBA	µg/kg	0	27	ND	ND	ND
DICHLOROPROP	µg/kg	0	27	ND	ND	ND
DIELDRIN	μg/kg	4	29	2.90	320.00	100.93
DIETHYL PHTHALATE	µg/kg	0	329	ND	ND	ND
DIMETHYL PHTHALATE	µg/kg	0	329	ND	ND	ND
DI-N-BUTYL PHTHALATE		20	329	30.00	570.00	197.35
DI-N-OCTYLPHTHALATE	µg/kg		329	67.00	67.00	67.00
DINOSEB	µg/kg	1	27	ND	ND	ND
/INCOLD	μg/kg	0	د ا	NU	LND	(Continu

Table 6-2 (Continued)		Т	T	T	1	T
Analyte	Units	# Detects	# Samples	Min.	Max.	Mean
DI-N-PROPYL ADIPATE	µg/kg	0	329	ND	ND	ND
ENDOSULFAN SULFATE	µg/kg	0	29	ND	ND	ND
ENDRIN	μg/kg	1	29	4.90	4.90	4.90
ENDRIN ALDEHYDE	μg/kg	0	29	ND	ND	ND
ENDRIN KETONE	μg/kg	1	29	4.20	4.20	4.20
ETHYLBENZENE	μg/kg	0	58	ND	ND	ND
FLUORANTHENE	μg/kg	43	329	16.00	770.00	104.19
FLUORENE	μg/kg	1	329	27.00	27.00	27.00
GAMMA BHC (LINDANE)	µg/kg	0	29	ND	ND	ND
GAMMA-CHLORDANE	µg/kg	0	29	ND	ND	ND
HEPTACHLOR	μg/kg	0	29	ND	ND	ND
HEPTACHLOR EPOXIDE	μg/kg	0	29	ND	ND	ND
HEPTACHLORINATED DIBENZOFURANS, (TOTAL)	pg/g	14	15	0.92	86.00	9.88
HEPTACHLORINATED DIBENZO-P-DIOXINS, (TOT	pg/g	15	15	14.00	82.00	39.13
HEXACHLORINATED DIBENZOFURANS, (TOTAL)	pg/g	15	15	0.23	34.00	6.83
HEXACHLORINATED DIBENZO-P-DIOXINS, (TOTA	pg/g	14	15	0.85	7.00	3.63
HEXACHLOROBENZENE	μg/kg	0	329	ND	ND	ND
HEXACHLOROBUTADIENE	μg/kg	0	329	ND	ND	ND
HEXACHLOROCYCLOPENTADIENE	µg/kg	0	329	ND	ND	ND
HEXACHLOROETHANE	μg/kg	0	329	ND	ND	ND
HEXAHYDRO-1,3,5-TRINITRO-1,3,5-TRIAZINE	μg/kg	26	711	14.00	15000.00	1121.08
INDENO(1,2,3-C,D)PYRENE	µg/kg	13	329	19.00	320.00	73.00
IRON	mg/kg	380	380	2050.00	34600.00	12934.1
ISOPHORONE	µg/kg	0	329	ND	ND	ND
LEAD	mg/kg	363	380	1.50	852.00	22.61
M,P-XYLENE (SUM OF ISOMERS)	μg/kg	0	21	ND	ND	ND
MAGNESIUM	mg/kg	380	380	155.00	8060.00	1467.37
MANGANESE	mg/kg	380	380	12.30	1570.00	96.58
MCPA	μg/kg	0	27	ND	ND	ND
MCPP	μg/kg	0	27	ND	ND	ND 0.07
MERCURY	mg/kg	83	380	0.01	1.70	0.07
METHOXYCHLOR	μg/kg	0	29	ND	ND 05.00	ND 0.70
METHYL ETHYL KETONE (2-BUTANONE)	µg/kg	27	58 58	3.00	25.00	9.70
METHYL ISOBUTYL KETONE (4-METHYL-2-PENTA	μg/kg	0	12	ND ND	ND ND	ND ND
METHYL TERT-BUTYL ETHER (MTBE)	μg/kg	0	58	ND	ND	ND
METHYLENE CHLORIDE	μg/kg %	12	12	2.00	52.50	24.82
MOISTURE MOLYBDENUM		156	364	0.10	22.70	0.79
	mg/kg	4	329	28.00	96.00	55.75
NAPHTHALENE NICKEL	μg/kg mg/kg	362	380	0.77	70.40	7.08
	mg/kg	8	8	0.33	7.20	2.48
NITRATE/NITRITE (AS N) NITROBENZENE	µg/kg	2	1040	48.00	120.00	84.00
NITROBENZENE NITROGEN, AMMONIA (AS N)	mg/kg	20	20	2.60	17.90	7.10
NITROGEN, AMMONIA (AS N) NITROGEN, NITRATE (AS N)	mg/kg	12	12	0.21	0.66	0.46
NITROGEN, NITRATE (AS N) NITROGLYCERIN	µg/kg	8	711	270.00	1300.00	706.25
N-NITROSODIMETHYLAMINE	µg/kg	0	329	ND	ND	ND
N-NITROSODIMETH LAMINE	μg/kg	0	329	ND	ND	ND
N-NITROSODI-N-PROPYLAMINE	µg/kg µg/kg	8	329	28.00	130.00	69.75
OCTACHLORODIBENZOFURAN	pg/g	14	15	0.97	36.00	7.71
OCTACHLORODIBENZO-P-DIOXIN	pg/g	15	15	250.00	5300.00	2168.67
		20	711	14.00	26000.00	3415.90
OCTAHYDRO-1,3,5,7-TETRANITRO-1,3,5,7-TET	µg/kg	•	21	ND	ND	ND
D-XYLENE (1,2-DIMETHYLBENZENE)	µg/kg	10	141	ואט	רואר	(Continu

Table 6-2 (Continued)	111	14 D-44	140	The:-	1 84	
Analyte	Units	# Detects	# Samples	Min.	Max.	Mean
PCB-1016 (AROCHLOR 1016)	µg/kg	0	37	ND	ND	ND
PCB-1221 (AROCHLOR 1221)	µg/kg	0	37	ND	ND	ND
PCB-1232 (AROCHLOR 1232)	µg/kg	0	37	ND	ND	ND
PCB-1242 (AROCHLOR 1242)	μg/kg	0	37	ND	ND	ND
PCB-1248 (AROCHLOR 1248)	μg/kg	0	37	ND	ND	ND
PCB-1254 (AROCHLOR 1254)	μg/kg	1	37	34.00	34.00	34.00
PCB-1260 (AROCHLOR 1260)	μg/kg	0	37	ND	ND	ND
PENTACHLORINATED DIBENZOFURANS, (TOTAL)	pg/g	15	15	0.49	30.00	13.97
PENTACHLORINATED DIBENZO-P-DIOXINS, (TOT	pg/g	12	15	0.33	1.00	0.72
PENTACHLOROPHENOL	µg/kg	2	356	18.00	140.00	79.00
PENTAERYTHRITOL TETRANITRATE	μg/kg	0	711	ND	ND	ND
PENTAERYTHRITOL TETRANITRATE	μg/L	0	94	ND	ND	ND
PERCHLORATE	μg/kg	34	676	1.70	75.40	8.32
PH	UNITS	7	7	4.80	5.20	5.03
PHENANTHRENE	μg/kg	21	329	18.00	200.00	66.00
PHENOL	μg/kg	3	329	20.00	28.00	23.67
PHOSPHORUS, TOTAL ORTHOPHOSPHATE (AS PO4	mg/kg	20	20	50.40	338.00	134.05
PICLORAM	μg/kg	0	27	ND	ND	ND
PICRIC ACID	μg/kg	0	709	ND	ND	ND
POTASSIUM	mg/kg	347	380	96.40	2310.00	644.80
PYRENE	μg/kg	43	329	17.00	740.00	107.37
SELENIUM	mg/kg	176	380	0.27	9.90	1.06
SILVER	mg/kg	37	380	0.15	1.70	0.49
SILVEX (2,4,5-TP)	µg/kg	0	27	ND	ND	ND
SODIUM	mg/kg	110	380	48.00	552.00	267.21
Solids, Percent	%	39	39	3	94.80	81.83
STYRENE	µg/kg	0	58	ND	ND	ND
SULFIDE	mg/kg	0	1	ND	ND	ND
TERT-BUTYL METHYL ETHER	μg/kg	0	31	ND	ND	ND
TETRACHLORINATED DIBENZOFURANS, (TOTAL)	pg/g	15	15	1.20	47.00	22.93
TETRACHLORINATED DIBENZO-P-DIOXINS, (TOT	pg/g	13	15	0.40	1.50	0.72
TETRACHLOROETHYLENE(PCE)	μg/kg	0	58	ND	ND	ND
TETRYL	μg/kg	2	711	30.00	32.00	31.00
THALLIUM	mg/kg	72	380	0.34	1.80	0.85
TOLUENE	μg/kg	9	58	0.80	3.70	1.80
TOTAL 1,2-DICHLOROETHENE	μg/kg	0	37	ND	ND	ND
TOTAL DICHLORINATED NAPHTHALENES	μg/kg	4	29	11.00	17000.00	4325.00
TOTAL HEPTACHLORINATED NAPHTHALENES	μg/kg	2	29	23.00	130.00	76.50
TOTAL HEXACHLORINATED NAPHTHALENES	μg/kg	3	29	16.00	3000.00	1138.67
TOTAL MONOCHLORINATED NAPHTHALENES	μg/kg	3	29	18.00	1700.00	579.00
TOTAL OCTACHLORINATED NAPHTHALENES	μg/kg	2	29	32.00	37.00	34.50
TOTAL ORGANIC CARBON	mg/kg	25	42	1180.00	37600.00	8115.60
TOTAL PENTACHLORINATED NAPHTHALENES	μg/kg	8	29	43.00	54000.00	7840.38
TOTAL TETRACHLORINATED NAPHTHALENES	μg/kg	8	29	67.00	330000.00	45821.50
TOTAL TRICHLORINATED NAPHTHALENES	μg/kg	8	29	31.00	310000.00	41365.13
TOXAPHENE	µg/kg	0	29	ND	ND	ND
TRANS-1,2-DICHLOROETHENE	μg/kg	0	15	ND	ND	ND
TRANS-1,2-DICHLOROETHYLENE	μg/kg	0	6	ND	ND	ND
TRANS-1,3-DICHLOROPROPENE	µg/kg	0	58	ND	ND	ND
TRICHLOROETHYLENE (TCE)	µg/kg	0	58	ND	ND	ND
/ANADIUM	mg/kg	380	380	4.10	76.60	22.50
	µg/kg	0	21	ND	ND	

Table 6-2 (Concluded)										
Analyte	Units	# Detects	# Samples	Min.	Max.	Mean				
VINYL CHLORIDE	μg/kg	0	58	ND	ND	ND				
WHITE PHOSPHORUS	μg/kg	0	3	ND	ND	ND				
XYLENES, TOTAL	μg/kg	0	58	ND	ND	ND				
ZINC	mg/kg	341	380	5.20	553.00	27.90				
ND – nondetectable					***					

Table 6-3				MANUA (* -		Alexander :
Summary of Camp Edwards Validated	Ground	water Dat	a from 1 C)ctobe	- 2003 tl	rough
30 August 2004	Oloulia	water but		,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,		oug
Analyte	Units	# Detects	# Samples	Min.	Max.	Mean
1-(METHYLAMINO) - ANTHRAQUINONE	µg/L	0	5	ND	ND	ND
1,1,1,2-TETRACHLOROETHANE	µg/L	0	3	ND	ND	ND
1.1.1-TRICHLOROETHANE	μg/L	0	307	ND	ND	ND
1.1.2.2-TETRACHLOROETHANE	µg/L	0	307	ND	ND	ND
1.1.2-TRICHLOROETHANE	μg/L	0	307	ND	ND	ND
1.1-DICHLOROETHANE	µg/L	0	307	ND	ND	ND
1.1-DICHLOROETHENE	µg/L	0	307	ND	ND	ND
1,1-DICHLOROPROPENE	µg/L	0	3	ND	ND	ND
1.2.3-TRICHLOROBENZENE	µg/L	0	3	ND	ND	ND
1,2,3-TRICHLOROPROPANE	µg/L	0	3	ND	ND	ND .
1,2,4-TRICHLOROBENZENE	µg/L	0	453	ND	ND	ND
1,2,4-TRIMETHYLBENZENE	µg/L	0	3	ND	ND	ND
1,2-DIBROMO-3-CHLOROPROPANE	µg/L	0	310	ND	ND	ND
1,2-DIBROMOETHANE (EDB)	μg/L	0	3	ND	ND	ND
1,2-DIBROMOETHANE (ETHYLENE DIBROMIDE)	μg/L	0	318	ND	ND	ND
1,2-DICHLOROBENZENE	µg/L	0	453	ND	ND	ND
1,2-DICHLOROETHANE	µg/L	0	307	ND	ND	ND
1,2-DICHLOROPROPANE	µg/L	0	307	ND	ND	ND
1,3,5-TRIMETHYLBENZENE (MESITYLENE)	μg/L	0	3	ND	ND	ND
1,3,5-TRINITROBENZENE	µg/L	1	1898	0.53	0.53	0.53
1,3-DICHLOROBENZENE	µg/L	0	453	ND	ND	ND
1,3-DICHLOROPROPANE	μg/L	0	3	ND	ND	ND
1,3-DIETHYL-1,3-DIPHENYL UREA	µg/L	0	155	ND	ND	ND
1,3-DINITROBENZENE	µg/L	0	1898	ND	ND	ND
1,4-BIS (P-TOLUIDINO) ANTHRAQUINONE	μg/L	0	5	ND	ND	ND
1,4-DIAMINO-2,3-DIHYDROANTHRAQUINONE	μg/L	0	5	ND	ND	ND
1,4-DICHLOROBENZENE	μg/L	2	453	0.20	0.30	0.25
2,2-DICHLOROPROPANE	μg/L	0	3	ND	ND	ND
2,2'-OXYBIS(1-CHLORO)PROPANE	μg/L	0	149	ND	ND	ND
2,4 DB	μg/L	0	64	ND	ND	ND
2,4,5-T (TRICHLOROPHENOXYACETIC ACID)	μg/L	0	64	ND	ND	ND
2,4,5-TRICHLOROPHENOL	μg/L	0	155	ND	ND	ND
2,4,6-TRICHLOROPHENOL	μg/L	0	155	ND	ND	ND
2,4,6-TRINITROTOLUENE	μg/L	13	1898	0.40	14.00	3.38
2,4-D (DICHLOROPHENOXYACETIC ACID)	μg/L	0	67	ND	ND	ND
2,4-DIAMINO-6-NITROTOLUENE	μg/L	1	1898	0.25	0.25	0.25
2,4-DICHLOROPHENOL	μg/L	0	155	ND	ND	ND
2,4-DIMETHYLPHENOL	μg/L	0	155	ND	ND	ND
2,4-DINITROPHENOL	μg/L	0	155	ND	ND	ND
2,4-DINITROTOLUENE	μg/L	5	2028	0.42	7.30	1.97

Analyte	Units	# Detects	# Samples	Min.	Max.	Mean
		+	T	+		
2,6-DIAMINO-4-NITROTOLUENE	μg/L	6	1898	ND 0.36	ND 1.10	ND 0.70
2,6-DINITROTOLUENE	µg/L	15	2028	0.36	1.10 2.60	0.70 1.01
2-AMINO-4,6-DINITROTOLUENE 2-CHLOROBENZALDEHYDE	μg/L	0	1898 155	ND	ND	ND
	µg/L	0	155		ND	ND
2-CHLOROBENZOIC ACID 2-CHLOROETHYL VINYL ETHER	μg/L	0	304	ND ND	ND	ND
2-CHLORONAPHTHALENE	µg/L	1	155	0.26	0.26	0.26
2-CHLOROPHENOL	μg/L	0	155	ND	ND	ND
2-CHLOROTOLUENE	μg/L μg/L	0	3	ND	ND	ND
2-ETHYLHEXYL ADIPATE		0	3	ND	ND	ND
2-HEXANONE	μg/L	0	304	ND	ND	ND
	µg/L	0	155	ND	ND ND	ND
2-METHYL-3-NITROANILINE	µg/L	0		ND	ND	ND
2-METHYL-5-NITROANILINE	µg/L		155			
2-METHYLNAPHTHALENE	µg/L	2	155	8.80	9.10	8.95
2-METHYLPHENOL (O-CRESOL)	µg/L	0	155	ND	ND	ND
2-NITROANILINE	µg/L	0	155	ND	ND	ND
2-NITRODIPHENYLAMINE	μg/L	0	155	ND	ND ND	ND
2-NITROPHENOL	μg/L	0	155	ND	ND	ND
2-NITROTOLUENE	μg/L	0	1898	ND	ND	ND
3,3'-DICHLOROBENZIDINE	µg/L	0	155	ND	ND	ND
3,5-DICHLOROBENZOIC ACID	μg/L	0	64	ND	ND	ND
3,5-DINITROANILINE	μg/L	0	155	ND	ND	ND
3-CHLOROBENZALDEHYDE	μg/L "	0	155	ND	ND	ND
3-NITROANILINE	μg/L	0	155	ND	ND	ND
3-NITROTOLUENE	µg/L	1	1898	0.29	0.29	0.29
4,6-DINITRO-2-METHYLPHENOL	µg/L	36	155	ND	ND 2.80	ND
4-AMINO-2,6-DINITROTOLUENE	µg/L		1898	0.26		0.88
4-BROMOPHENYL PHENYL ETHER 4-CHLORO-3-METHYLPHENOL	µg/L	0	155 155	ND ND	ND ND	ND ND
4-CHLOROANILINE	µg/L	0	155	ND	ND	ND
4-CHLOROBENZALDEHYDE	µg/L	0	155	ND	ND	ND
4-CHLOROBENZALDERTDE 4-CHLOROPHENYL PHENYL ETHER	µg/L	0	155	ND	ND	ND
4-CHLOROTOLUENE	μg/L	0	3	-	ND	ND
	µg/L	0	155	ND ND	ND	ND
4-METHYLPHENOL (P-CRESOL) 4-NITROANILINE	μg/L μg/L	0	155	ND	ND	ND
		0	219	 	ND	ND
4-NITROPHENOL 4-NITROTOLUENE	µg/L	0	1898	ND ND	ND	ND
ACENAPHTHENE	μg/L	2	155	0.46	0.59	0.53
ACENAPHTHYLENE	µg/L	0	155	ND	ND	ND
ACETONE	μg/L	26	304	2.00	20.00	5.80
ACIFLUORFEN	μg/L μg/L	0	64	ND	ND	ND
ALACHLOR	μg/L μg/L	0	3	ND	ND	ND
ALDRIN	µg/L	0	14	ND	ND	ND
ALKALINITY, BICARBONATE (AS CACO3)	mg/L	11	11	6.80	25.30	14.48
ALKALINITY, CARBONATE (AS CACOS)	mg/L	0	11	ND	ND	ND
ALKALINITY, HYDROXIDE (AS CACO3)	mg/L	0	11	ND	ND	ND
ALKALINITY, TOTAL (AS CACOS)	mg/L	11	11	6.80	25.30	14.48
ALPHA BHC (ALPHA HEXACHLOROCYCLOHEXANE)	µg/L	0	11	ND	ND	ND
ALPHA ENDOSULFAN	µg/L	0	11	ND	ND	ND
ALPHA, GROSS	pci/L	2	7	1.50	2.10	1.80
ALPHA-CHLORDANE	µg/L	2	11	0.01	0.01	0.01
ALUMINUM	————	8	83	53.90	3340.00	676.11
LOWINGIVI	µg/L	٥	Los	L 99.80	L3340.00	(Continu

Table 6-3 (Continued)						T
Analyte	Units	# Detects	# Samples	Min.	Max.	Mean
ANILINE	μg/L	0	155	ND	ND	ND
ANTHRACENE	µg/L	0	155	ND	ND	ND
ANTIMONY	µg/L	0	167	ND	ND	ND
ARSENIC	µg/L	4	86	4.10	27.80	16.22
ATRAZINE	μg/L	0	3	ND	ND	ND
BARIUM	μg/L	19	86	2.10	112.00	30.12
BENTAZON	μg/L	0	64	ND	ND	ND
BENZANTHRONE	µg/L	0	5	ND	ND	ND
BENZENE	µg/L	6	307	0.20	140.00	43.52
BENZO(A)ANTHRACENE	µg/L	0	155	ND	ND	ND
BENZO(A)PYRENE	μg/L	1	158	0.50	0.50	0.50
BENZO(B)FLUORANTHENE	µg/L	1	155	0.44	0.44	0.44
BENZO(G,H,I)PERYLENE	μg/L	1	155	0.25	0.25	0.25
BENZO(K)FLUORANTHENE	µg/L	1	155	0.42	0.42	0.42
BENZOIC ACID	μg/L	2	155	0.96	1.00	0.98
BENZYL ALCOHOL	µg/L	0	155	ND	ND	ND
BENZYL BUTYL PHTHALATE	µg/L	0	155	ND	ND	ND
BERYLLIUM	μg/L	6	86	0.34	0.63	0.44
BETA BHC (BETA HEXACHLOROCYCLOHEXANE)	µg/L	0	11	ND	ND	ND
BETA ENDOSULFAN	µg/L	0	11	ND	ND	ND
BIS(2-CHLOROETHOXY) METHANE	µg/L	0	155	ND	ND	ND
BIS(2-CHLOROETHYL) ETHER (2-CHLOROETHYL	µg/L	0	155	ND	ND	ND
BIS(2-CHLOROISOPROPYL) ETHER	µg/L	0	6	ND	ND	ND
BIS(2-ETHYLHEXYL) PHTHALATE	µg/L	31	158	0.23	4.90	0.83
BORON	µg/L	56	83	3.10	44.70	10.59
BROMOBENZENE	µg/L	0	3	ND	ND	ND
BROMOCHLOROMETHANE	µg/L	0	307	ND	ND	ND
BROMODICHLOROMETHANE	µg/L	0	307	ND	ND	ND
BROMOFORM	µg/L	0	307	ND	ND	ND
BROMOMETHANE	μg/L	0	307	ND	ND	ND
BUTACHLOR	µg/L	0	3	ND	ND	ND
CADMIUM	μg/L	2	86	1.40	1.40	1.40
CALCIUM	μg/L	83	83	680.00	9600.00	2517.41
CARBAZOLE	µg/L	0	155	ND	ND	ND
CARBON DISULFIDE	μg/L	3	304	0.20	0.56	0.32
CARBON TETRACHLORIDE	μg/L	0	307	ND	ND	ND
CHLORAMBEN	µg/L	0	64	ND	ND	ND
CHLORDANE	μg/L	0	3	ND	ND	ND
CHLORIDE (AS CL)	mg/L	11	11	5.50	10.10	7.55
CHLOROBENZENE	µg/L	1	307	0.40	0.40	0.40
CHLOROETHANE	µg/L	2	307	2.00	3.00	2.50
CHLOROFORM	µg/L	239	307	0.20	5.00	1.11
CHLOROMETHANE	µg/L	25	307	0.20	33.00	2.07
CHROMIUM, TOTAL	μg/L	6	86	1.30	10.80	4.95
CHRYSENE	µg/L	0	155	ND	ND	ND
CIS-1,2-DICHLOROETHENE	µg/L	0	3	ND	ND	ND
CIS-1,2-DICHLOROETHYLENE	μg/L	0	304	ND	ND	ND
CIS-1,3-DICHLOROPROPENE	µg/L	0	307	ND	ND	ND
COBALT	μg/L	2	83	17.20	21.20	19.20
COPPER	μg/L	13	83	1.60	232.00	41.12
CYANIDE	µg/L	0	8	ND	ND	ND
CYANIDE	mg/L	0	3	ND	ND	ND
	13	•			, <u>*</u>	(Continue

Table 6-3 (Continued)						
Analyte	Units	# Detects	# Samples	Min.	Max.	Mean
DALAPON	μg/L	0	67	ND	ND	ND
DCPA (DACTHAL)	μg/L	0	64	ND	ND	ND
DDD (1,1-BIS(CHLOROPHENYL)-2,2-DICHLOROE	μg/L	0	11	ND	ND	ND
DDE (1,1-BIS(CHLOROPHENYL)-2,2-DICHLOROE	μg/L	0	11	ND	ND	ND
DDT (1,1-BIS(CHLOROPHENYL)-2,2,2-TRICHLO	μg/L	0	11	ND	ND	ND
DELTA BHC (DELTA HEXACHLOROCYCLOHEXANE)	μg/L	0	11	ND	ND	ND
DIBENZ(A,H)ANTHRACENE	μg/L	0	155	ND	ND	ND
DIBENZOFURAN	μg/L	0	155	ND	ND	ND
DIBROMOCHLOROMETHANE	μg/L	0	307	ND	ND	ND
DIBROMOMETHANE	μg/L	0	307	ND	ND	ND
DICAMBA	μg/L	0	67	ND	ND	ND
DICHLORODIFLUOROMETHANE	µg/L	0	3	ND	ND	ND
DICHLOROPROP	μg/L	0	64	ND	ND	ND
DIELDRIN	μg/L	0	14	ND	ND	ND
DIETHYL PHTHALATE	μg/L	2	155	0.45	0.55	0.50
DIMETHYL PHTHALATE	μg/L	0	155	ND	ND	ND
DI-N-BUTYL PHTHALATE	μg/L	1	155	0.25	0.25	0.25
DI-N-OCTYLPHTHALATE	μg/L	1	155	0.80	0.80	0.80
DINOSEB	μg/L	0	67	ND	ND	ND
DI-N-PROPYL ADIPATE	μg/L	0	155	ND	ND	ND
ENDOSULFAN SULFATE	μg/L	0	11	ND	ND	ND
ENDRIN	μg/L	0	14	ND	ND	ND
ENDRIN ALDEHYDE	μg/L	0	11	ND	ND	ND
ENDRIN KETONE	μg/L	0	11	ND	ND	ND
ETHYLBENZENE	μg/L	5	307	0.30	82.00	33.06
FLUORANTHENE	µg/L	0	155	ND	ND	ND
FLUORENE	μg/L	2	155	1.50	1.90	1.70
GAMMA BHC (LINDANE)	µg/L	0	14	ND	ND	ND
GAMMA-CHLORDANE	μg/L	2	11	0.01	0.01	0.01
HARDNESS (AS CACO3)	mg/L	1	82	42.20	42.20	42.20
HEPTACHLOR	μg/L	0	14	ND	ND	ND
HEPTACHLOR EPOXIDE	μg/L	0	14	ND	ND	ND
HEXACHLOROBENZENE	μg/L	0	158	ND	ND	ND
HEXACHLOROBUTADIENE	μg/L	0	158	ND	ND	ND
HEXACHLOROCYCLOPENTADIENE	μg/L	0	158	ND	ND	ND
HEXACHLOROETHANE	μg/L	0	155	ND	ND	ND
HEXAHYDRO-1,3,5-TRINITRO-1,3,5-TRIAZINE	μg/L	415	1898	0.25	220.00	6.33
HEXAHYDRO-1,3,5-TRINITROSO-1,3,5-TRIAZIN	μg/L	0	122	ND	ND	ND
HEXAHYDRO-1,3-DINITROSO-5-MONONITRO-1,3,	µg/L	0	122	ND	ND	ND
HEXAHYDRO-1-MONONITROSO-3,5-DINITRO-1,3,	μg/L	6	122	0.26	0.97	0.54
INDENO(1,2,3-C,D)PYRENE	µg/L	1	155	0.27	0.27	0.27
RON	μg/L	26	83	34.40	106000	8500.81
SOPHORONE	μg/L	0	155	ND	ND	ND
SOPROPYLBENZENE (CUMENE)	µg/L	0	3	ND	ND 50.70	ND 10
EAD	µg/L	9	86	1.40	50.70	13.13
M,P-XYLENE (SUM OF ISOMERS)	µg/L	0	15	ND	ND 5490.00	ND
MAGNESIUM	µg/L	82	83	381.00	5480.00	1537.90
MANGANESE	µg/L	60	83	1.20	1580.00	84.27
MCPA	µg/L	0	64	ND	ND	ND
MCPP	µg/L	0	64	ND 0.00	ND	ND
MERCURY	μg/L	1	83	0.28	0.28	0.28
MERCURY	mg/L	0	3	ND	ND	ND (Continued

Table 6-3 (Continued)						
Analyte	Units	# Detects	# Samples	Min.	Max.	Mean
METHOXYCHLOR	µg/L	0	14	ND	ND	ND
METHYL ETHYL KETONE (2-BUTANONE)	μg/L	12	304	1.00	10.00	3.08
METHYL ISOBUTYL KETONE (4-METHYL-2-PENTA	μg/L	1	304	22.00	22.00	22.00
METHYL TERT-BUTYL ETHER (MTBE)	μg/L	1	3	1.80	1.80	1.80
METHYLENE CHLORIDE	µg/L	0	307	ND	ND	ND
METOLACHLOR	μg/L	0	3	ND	ND	ND
METRIBUZIN	μg/L	0	3	ND	ND	ND
MOLYBDENUM	μg/L	5	83	1.50	7.20	2.88
M-XYLENE (1,3-DIMETHYLBENZENE)	μg/L	0	3	ND	ND	ND
NAPHTHALENE	μg/L	2	158	15.00	16.00	15.50
N-BUTYLBENZENE	μg/L	0	3	ND	ND	ND
NICKEL	μg/L	7	86	1.40	17.00	4.80
NITRATE/NITRITE (AS N)	mg/L	7	11	0.01	0.34	0.09
NITROBENZENE	μg/L	0	2028	ND	ND	ND
NITROGEN, AMMONIA (AS N)	mg/L	3	11	0.04	0.05	0.05
NITROGEN, NITRATE (AS N)	mg/L	0	3	ND	ND	ND
NITROGEN, NITRITE	mg/L	0	3	ND	ND	ND
NITROGLYCERIN	µg/L	0	1898	ND	ND	ND
N-NITROSODIMETHYLAMINE	μg/L	0	155	ND	ND	ND
N-NITROSODI-N-PROPYLAMINE	µg/L	0	155	ND	ND	ND
N-NITROSODIPHENYLAMINE	μg/L	0	155	ND	ND	ND
N-PROPYLBENZENE	μg/L	0	3	ND	ND	ND
OCTAHYDRO-1,3,5,7-TETRANITRO-1,3,5,7-TET	μg/L	169	1898	0.25	110	5.38
O-XYLENE (1,2-DIMETHYLBENZENE)	μg/L	0	18	ND	ND	ND
PCB-1016 (AROCHLOR 1016)	μg/L	0	14	ND	ND	ND
PCB-1221 (AROCHLOR 1221)	μg/L	0	14	ND	ND	ND
PCB-1232 (AROCHLOR 1232)	μg/L	0	14	ND	ND	ND
PCB-1242 (AROCHLOR 1242)	μg/L	0	14	ND	ND	ND
PCB-1248 (AROCHLOR 1248)	μg/L	0	14	ND	ND	ND
PCB-1254 (AROCHLOR 1254)	μg/L	0	14	ND	ND	ND
PCB-1260 (AROCHLOR 1260)	μg/L	0	14	ND	ND	ND
P-CYMENE (P-ISOPROPYLTOLUENE)	μg/L	0	3	ND	ND	ND
PENTACHLOROPHENOL	μg/L	0	222	ND	ND	ND
PENTAERYTHRITOL TETRANITRATE	μg/L	0	1898	ND	ND	ND
PERCHLORATE	μg/L	606	2585	0.18	494	7.34
PHENANTHRENE	μg/L	2	155	1.60	2.20	1.90
PHENOL	μg/L	3	155	0.26	0.80	0.57
PHOSPHORUS, TOTAL ORTHOPHOSPHATE (AS PO4	mg/L	8	11	0.03	0.09	0.05
PICLORAM	μg/L	0	67	ND	ND	ND
PICRIC ACID	μg/L	1	1898	0.48	0.48	0.48
POTASSIUM	μg/L	45	83	196	6790	1131.1
PROPACHLOR	µg/L	0	3	ND	ND	ND
P-XYLENE (1,4-DIMETHYLBENZENE)	μg/L	0	3	ND	ND	ND
PYRENE	µg/L	0	155	ND	ND	ND
SEC-BUTYLBENZENE	μg/L	0	3	ND	ND	ND
SELENIUM	µg/L	0	86	ND	ND	ND
SILVER	µg/L	1	83	2.10	2.10	2.10
SILVEX (2,4,5-TP)	µg/L	0	67	ND	ND	ND
SIMAZINE	µg/L	0	3	ND	ND	ND
SODIUM	µg/L	82	83	2420	77200	8921.8
SODIUM	mg/L	3	3	5.80	11.00	7.97
STYRENE		,	307	ND	ND	ND

Table 6-3 (Concluded)						
Analyte	Units	# Detects	# Samples	Min.	Max.	Mean
SULFATE (AS SO4)	mg/L	12	12	1.90	6.30	3.97
T-BUTYLBENZENE	μg/L	0	3	ND	ND	ND
TERT-BUTYL METHYL ETHER	μg/L	6	152	0.20	0.70	0.44
TETRACHLOROETHENE(PCE)	μg/L	0	3	ND	ND	ND
TETRACHLOROETHYLENE(PCE)	μg/L	3	304	0.20	1.00	0.73
TETRYL	μg/L	0	1898	ND	ND	ND
THALLIUM	μg/L	0	167	ND	ND	ND
TOLUENE	μg/L	17	307	0.20	37	44.75
TOTAL ORGANIC CARBON	mg/L	0	11	ND	ND	ND
TOXAPHENE	μg/L	0	14	ND	ND	ND
TRANS-1,2-DICHLOROETHENE	μg/L	0	303	ND	ND	ND
TRANS-1,2-DICHLOROETHYLENE	μg/L	0	4	ND	ND	ND
TRANS-1,3-DICHLOROPROPENE	μg/L	0	307	ND	ND	ND
TRICHLOROETHENE(TCE)	μg/L	0	3	ND	ND	ND
TRICHLOROETHYLENE (TCE)	µg/L	6	304	0.20	2.00	1.17
TRICHLOROFLUOROMETHANE	µg/L	0	3	ND	ND	ND
VANADIUM	μg/L	1	83	4.90	4.90	4.90
VINYL ACETATE	μg/L	0	304	ND	ND	ND
VINYL CHLORIDE	μg/L	0	307	ND	ND	ND
XYLENES, TOTAL	μg/L	4	307	23.00	720.00	352.00
ZINC	μg/L	25	83	2.50	38.50	14.10

ND - nondetectable

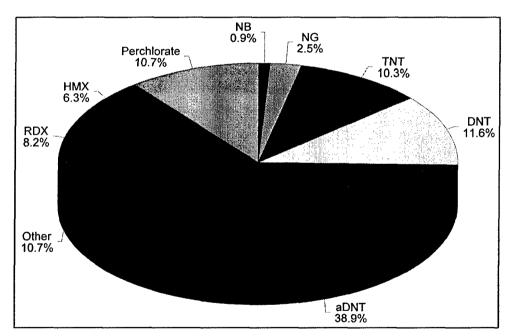


Figure 6-1. Distribution of MEC compounds in soil at Camp Edwards for the dataset running from 1 October 2003 to 30 August 2004

The soil MEC compound findings are consistent with known activities at Camp Edwards, such as the firing of munitions-containing mixtures of TNT, RDX, HMX, and PCNs in the warheads, and propellants with nitroglycerine (NG), DNT, di-n-butyl phthalate, and N-nitrosodiphenylamine. The presence of the aDNTs is strongly suggestive of the aerobic transformation of TNT.

In contrast, the distribution of MEC in groundwater (Figure 6-3) is different from soil but consistent with previous groundwater findings as reported in Pennington et al. (2003). The predominant MEC observed in Camp Edwards groundwater is perchlorate, followed by RDX, HMX, and aDNTs in decreasing order of frequency. The greater preponderance of RDX and perchlorate can be explained by their conservative behavior relative to the other contaminants. As a consequence of RDX's and perchlorate's high solubility, low to nonexistent partitioning to soil, and recalcitrant nature, they are not expected to persist in soil for any significant length of time once in solution. Rather, once in contact with precipitation, perchlorate will rapidly dissolve and then be transported down through the unsaturated zone to the water table. In contrast, the dissolution kinetics of RDX are much slower, such that RDX will persist in soil as a solid for a significant length of time (decades to centuries). The significant decrease in TNT and aDNTs in groundwater relative to soil is a function of their susceptibility to transformation processes and sorption onto shallow surface soils. Even when the TNT and aDNT levels suppress the natural microorganisms in the soil, these compounds are rapidly transformed within several hundred feet of where they are introduced into the aquifer.

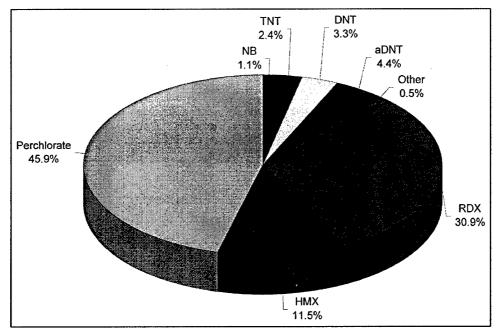


Figure 6-3. Distribution of MEC compounds in groundwater at Camp Edwards for the dataset running from 1 October 2003 to 30 August 2004

The majority of DNT observed in soil is the 2,4 isomer, whereas in ground-water it is the 2,6 isomer. This same phenomenon continues to be observed in FY04 data from Camp Edwards. This difference may be a function of differences in mobility for the various DNT isomers. The Impact Area Groundwater Study has also found that false positives of 2,6-DNT occur in groundwater samples, especially when interferences are present. It is possible that the infrequent and sporadic 2,6-DNT detections observed in groundwater samples, which are not reproducible between different sampling events, are false positives.

The other important observation is the significant decrease of "Other" compounds and the lack of NG in groundwater relative to soil. N-nitrosodiphenylamine and PCN are two of the "Other" compounds that have not been detected in any groundwater samples. The absence of N-nitrosodiphenylamine, NG, and PCNs is consistent with their fate and transport properties, i.e. rapid and strong sorption to soil, low solubility, and high degradation potential. The absence of NG in groundwater can also be attributed to the fact that it is embedded in nitrocellulose fibers, which hinders contact with water and thus dissolution. Di-nbutyl phthalate and di-n-octyl phthalate are the "Other" compounds detected in groundwater. The phthalates are not mobile because of their affinity for soils and thus are not expected in groundwater. The detection of phthalates in groundwater has been spatially sporadic and nonreproducible between sampling rounds for the same monitoring well. Phthalates are a common laboratory contaminant, and the detections in groundwater may represent false positives. Di-n-butyl phthalate and di-n-octyl phthalate are found in propellants, the presence of which is expected in soil at locations where propellant was handled and fired, such as the mortar, artillery, and rocket firing positions. Their presence at other sites, such as the Impact Area where propellants are not likely to be present, is viewed with some uncertainty. Phthalates observed in the absence of the DNTs and N-nitrosodiphenylamine may represent false positives. In contrast, if DNT and N-nitrosodiphenylamine are present along with the phthalates, then the phthalates likely represent propellant residues. The DNTs and diphenylamine, which oxidize to Nnitrosodiphenylamine, are major constituents in the propellants that contain di-nbutyl phthalate and di-n-octyl phthalate.

Long-Term Groundwater Monitoring Program

The Camp Edwards groundwater monitoring program has been in existence since 1997. AMEC published the 2004 annual review and plan for long-term monitoring on 13 May 2004 (AMEC 2004a). The 2004 plan included several major improvements. The objectives and future direction of the monitoring program were re-evaluated to keep pace with the evolving needs of the maturing area investigations. AMEC developed a new approach, shifting the monitoring plan designs from characterization-focused monitoring to remediation-focused monitoring. This revision includes organizing monitoring wells by operable unit, categorizing each monitoring well based on its specific objectives, conducting statistical reviews of metals and herbicides data, and developing extensive drawings including cross-sections for known contamination areas. As remedial systems are installed, operable-unit-specific sections of the long-term monitoring plan will be replaced by operational monitoring plans such as the Groundwater System Performance and Ecological Impact Monitoring Plan (AMEC 2004b), which is scheduled to replace the long-term monitoring plan for Demo 1 starting with the December 2004 event.

Since its inception in 1997, the Camp Edwards monitoring program has grown to include over 800 wells distributed geographically over eight areas of interest. Currently, the Impact Area and Southeast Ranges account for the largest number of wells in the long-term monitoring plan, with approximately 230 wells monitored per area. One hundred wells are used to monitor groundwater quality at the Demo 1 operable unit, 90 wells are located in the Western Boundary oper-

able unit, and the remaining 165 wells monitor smaller operable units. AMEC collects samples from these wells from one to three times per year, based on the well's location relative to groundwater contaminant plumes and in accordance with input from both state and federal regulators. Supply wells and wells immediately up-gradient (sentinel wells) are monitored four times per year. The 2004 long-term monitoring plan includes the collection of approximately 1,300 explosives water samples, 1,470 perchlorate samples, 105 metals samples, 120 semivolatile organic compounds (SVOCs) samples, and 160 volatile organic compounds (VOCs) samples. In addition, selected wells are analyzed for pesticides (three analyses), dyes (four analyses), and drinking water parameters (four analyses) based on well-specific concerns.

After installation of a new well, groundwater samples are collected for three sampling events based on parameters specified in the varying operable unit work plans. Available data from new wells are reviewed prior to the start of each trimester sampling event, and recommendations are made for inclusion in the long-term monitoring plan. As part of the ongoing review of these new wells, 15 wells were reviewed and added to the long-term monitoring plan for the August 2004 event, and approximately 20 wells will be added to the long-term monitoring plan as part of the December 2004 review.

Impact Area

The Impact Area is located in the central portion of Camp Edwards and covers 2,200 acres. Within the Impact Area is a 330-acre area identified as the Central Impact Area, where the major source of groundwater contamination is located. Surrounding the Impact Area are a number of ranges and firing positions from which artillery and mortar rounds were fired.

A total of 319 monitoring wells at 126 locations have been installed within and down-gradient of the Impact Area. In excess of 1,000 groundwater profile and 1,500 groundwater monitoring well samples have been collected and analyzed for explosives and VOCs.

Soil

Characterization of the nature and extent of the MEC in the Central Impact Area is nearing completion. During the past year, a focused soil investigation was conducted around Targets 23 and 42 located within the Central Impact Area. Previous soil sampling efforts had identified these two areas as being the most heavily contaminated with HE based on frequency of HE detection and maximum concentration of HE (AMEC 2001a). Composite soil sample grids using eight increments were established using a 22-ft spacing extending away from the target for a distance of 500 ft. The expectation was that HE concentrations would decrease with distance. However, at T42, samples immediately adjacent to the target indicated the presence of HE followed by a series of grids with no detectable HE and then more grids with HE present. At Target 23, no HE was detected in any of the soil samples collected. A third round of soil sampling conducted in

conjunction with ERDC/CRREL using composites of 30–100 increments revealed HE at levels consistently above 1 ppm at T42 and approximately 100 ppb at T23. The discrepancy between soil sampling rounds is likely attributable to differences in sampling methodologies. The ERDC/CRREL sampling methods included larger sample aliquots, more increments per composite sample, and no removal of organic material from the soil sample. It is believed that the earlier soil sampling rounds using five- and eight-increment composites did not provide results representative of site conditions.

In addition to soil sampling, a series of tension lysimeters were installed in groups of three at three locations and three depths around each target. Lysimeters at both T23 and T42 yielded water samples containing HE, including those installed at Target 23, where the second round of soil sampling indicated no detectable HE residues. A report documenting these results is being prepared.

In addition, AMEC is preparing a soil report discussing all characterization efforts to date within the Central Impact Area. The preliminary assessment of the data indicates that the source term for groundwater is confined to an area of approximately 330 acres. A total of 58 targets fired on from the Gun and Mortar positions have been investigated in the Central Impact Area. More than 3,500 soil samples have been collected to date and analyzed for some or all of the following parameters: explosives, metals, SVOCs, herbicides, pesticides, VOCs, cyanide, phosphate, nitrate, ammonia, perchlorate, polychlorinated biphenyls (PCBs), and PCNs (AMEC 2001). The compounds 2-amino-4,6-dinitrotoluene (2a-DNT), 4-amino-2,6-dinitrotoluene (4a-DNT), TNT, and RDX have been identified as soil contaminants of concern (COCs) for the Central Impact Area based on a human health risk assessment (AMEC 2001).

Groundwater

The compounds RDX, 2,4-DNT, and 4a-DNT have been identified as groundwater COCs for the Impact Area based on human risk characterization (ÅMEC 2001b). RDX concentrations found in groundwater samples are generally less than 10 μ g/L but greater than 2 μ g/L, the EPA health advisory limit. Reverse particle backtracks using a site groundwater model indicate that a distributed source area is located primarily in the vicinity of the targets along and east of Turpentine Road. HMX and perchlorate groundwater contamination is generally co-located with that of RDX.

The Impact Area groundwater plume covers an area approximately 16,000 ft long by 5,000 ft wide. Approximately 880 million to 1.3 billion gallons of water have been contaminated, encompassing an area of 2.5 km² (621 acres). The amount of RDX dissolved in this volume of contamination is approximately 30-80 lbs (AMEC 2001b). The maximum observed groundwater concentration of RDX was 32 μ g/L. No explosive compounds have been detected in groundwater beyond the western perimeter of the MMR property boundary linked to the Impact Area.

Demolition Area 1

Demolition Area 1 (Demo 1) is located south of the Impact Area at Camp Edwards in a one-acre kettle hole, with the bottom 45 ft below the surrounding grade. Demolition and explosive, ordnance, and disposal (EOD) training at Demo 1, as well as OB/OD operations, began sometime in the mid-1970s and included the destruction of various types of ordnance using explosive charges of C4, TNT, and detonation cord. As part of a comprehensive site reconnaissance, chunks of C4 and other residual munitions were found on the ground surface and removed in accordance with approved procedures, which typically consisted of detonation in the Closed Detonation Chamber located on site.

Soil

Over 600 soil samples have been collected at Demo 1. The following explosive and propellant compounds have been repeatedly detected in soil and groundwater at Demo 1: perchlorate, RDX, HMX, 2a-DNT, 4a-DNT, TNT, and 2.4-DNT (AMEC 2001c, 2003c). RDX (22 percent) and HMX (13 percent) were the most frequently detected explosive compounds. A maximum concentration of 14,000 mg/kg of RDX was measured in the soil below a chunk of Composition (C4) resting on the soil surface, indicating that particulates were present in this soil sample. The average concentration of RDX in soil, using one-half the detection limit for non-detects and excluding three sample locations collected beneath C4 residuals, was 0.576 mg/kg. Trinitrotoluene (TNT) was also heavily used in demolition training. The low frequency of TNT detection (2 percent) in soil is most likely due to the rapid degradation of TNT to the daughter products 2a-DNT (7 percent) and 4a-DNT (5 percent). The principal transformation products of TNT are 2a-DNT, 4a-DNT, and 2,6-DANT. 2,4-DNT and 2,6-DNT are not transformation products, but are components of propellants and impurities in TNT manufacturing.

A Draft Rapid Response Action (RRA) Plan was prepared by AMEC and submitted to the EPA and MADEP on 19 February 2003. The plan presented the conceptual design of voluntary interim actions to reduce or eliminate potential risks to human health present at Demo 1 as a result of historic OB/OD, disposal, and demolition training activities.

Low-temperature thermal desorption (LTTD) was the selected remedial alternative for treatment of soil contaminated with explosives and propellants. The site characterization data showed that COC were co-located, and RDX was detected most frequently and at the highest concentrations. Also, RDX and perchlorate are the primary contaminants in groundwater at Demo 1. Therefore, RDX and perchlorate were targeted for remediation and confirmation sampling subsequent to excavation.

Several activities were conducted in preparation of soil treatment via LTTD, including preparation of a soil treatment plan, construction of a soil treatment facility, completion of a treatability study and associated reporting, completion of a proof of performance test and associated reporting, and air permitting as

required by the Massachusetts Department of Environmental Protection (MADEP). Prior to soil excavation, unexploded ordnance (UXO) clearance and anomaly removal activities were conducted at Demo 1. UXO clearance activities began in June 2003, and UXO and anomaly removal activities have been conducted concurrently with excavation of soil, as safety allowed. Excavation of soil began in February 2004 and was completed in September 2004. The Thermal Treatment Unit treated approximately 25,000 tons of contaminated soil from Demo 1. Treated soil has been stockpiled on-site and will be returned to the site during restoration activities. Sampling of treated soil was conducted to ensure destruction of contaminants, and post-excavation confirmation samples were collected to demonstrate achievement of remediation goals.

AMEC prepared a Draft Final Environmental Risk Characterization for the Demo 1 Soil operable unit (AMEC 2004b). The report assesses the ecological risk present at the site prior to remedial activities and includes site-specific bioaccumulation information acquired during field biota sampling and analyses. AMEC is currently awaiting comments from EPA and MADEP.

Groundwater

Ninety-eight monitoring wells at 36 locations have been installed at Demo 1. Over 1,800 groundwater samples have been collected and analyzed for explosives and/or perchlorate. Using these data as well as data collected by pneumatic slug testing methods, a revised conceptual model was completed this fiscal year.

A groundwater containment system for the Demo 1 plume was designed and is starting up in September 2004 as a groundwater RRA. This interim action addresses groundwater contaminated with explosive compounds and perchlorate. The objective of the interim action is to provide hydraulic capture of most of the groundwater plume to control further migration and to initiate removal and treatment of dissolved contaminant mass contained within the plume. The system will use granular activated carbon (GAC) and ion exchange (IX) resin to treat contaminated groundwater, which will later be disposed offsite in a landfill or regenerated.

In the Feasibility Study (FS) completed this year, groundwater modeling and an innovative particle tracking optimization program were used to identify the most efficient extraction well locations and pumping rates required to meet project objectives. The approach for the FS is to focus on the extraction well locations and pumping rates while providing a conceptual groundwater treatment system design to facilitate regulatory and public approval. An optimization methodology approach, Brute Force within Groundwater Vistas (Rumbaugh and Rumbaugh 1997), was used for determining the most efficient remedial scheme for containing or collapsing a groundwater plume of explosive compounds and perchlorate and to conceptualize potential remedial alternatives. Groundwater modeling tools such as MODFLOW and MODPATH (McDonald and Harbough 1988, Pollack 1994) were used to assist the decision making process of monitoring well placement and screen settings, including the installation of extraction and reinjection wells.

Partial agency comments have been received and are being incorporated into a Memorandum of Resolution (MOR) for the FS. A Remedy Selection Plan for the comprehensive remedy is being drafted.

Demolition Area 2

Demolition Area 2 (Demo 2) was used from the late 1970s to the late 1980s for light demolition training. Records indicate that explosive charges including C-4, TNT (in quantities less than 10 pounds), and claymore mines were used. A subsurface geophysical survey was conducted at the Demo 2 area in September 2001. The area investigated was 190 m long and 60 m wide (approximately 3 acres), and was surface-cleared of any metal or other objects. Materials recovered from the surveyed areas consisted of scrap metal and barbed wire. No UXO were discovered during the geophysical survey.

Soil

Results for analyses of soil samples collected from the perimeter berm revealed the presence of four explosive compounds: RDX, HMX, 2A-DNT, and 4A-DNT. Nearly all of the compounds were detected in nine samples collected from Trenches 2 and 4 and associated spoils piles. Trench 1 samples exhibited a single detection of RDX. The maximum concentrations of RDX and HMX (3,000 and an estimated value of 300 μ g/kg, respectively) were reported in samples collected from Trench 2. The maximum concentrations of the TNT transformation products 2A-DNT and 4A-DNT (42 and 28 μ g/kg, respectively) were reported in samples obtained from Trench 4.

Remnant bulk explosive chunks (both TNT and C4) associated with past engineer training activities were found at Demo 2 and are assumed to be the source of residual RDX, HMX, 2A-DNT, and 4A-DNT in soil. Because of the potential presence of additional bulk explosives chucks in the perimeter berm, an RRA soil removal was performed. Approximately 750 cubic yards of soil were excavated, removed from the site, and processed through the on-site LTTD.

Groundwater

Nine monitoring well locations have been installed in the Demo 2 area. RDX and HMX have been detected in groundwater. The initial assessment is that at least 3,200 ft of downgradient migration has occurred. RDX concentrations ranged from 0.49 to $2.8~\mu g/L$.

Southeast Ranges

The SE Ranges consist of four ranges used by defense contractors for munitions testing, including research and development activities. The J-1 Range was used primarily as an estimation, anti-tank, and transition range from the

mid-1930s through the 1950s. The J-1 Range was subsequently used until the 1980s for weapons testing by a variety of military contractors.

The original J-2 Range was established in the late 1940s in an area currently designated as N Range. The J-2 Range was used historically as a musketry range (1935 to 1940s), transition range (1940s to 1950s), rifle range (1960s to 1980s), and contractor test range (1953 to 1980). Examples of activities conducted by various contractors included propellant and fuze testing, penetration testing for various munitions, fragmentation testing, smoke testing, infrared testing of tank heat signatures, propellant and waste burning, munitions disposal, and loading of munitions with HE.

The J-3 Range was used for mortar and machine gun practice from 1935 through the 1950s. Textron, Inc., under various military contracts, used the range from 1968 to the 1990s for loading and testing various munitions and fuzes and a wide variety of other munitions-related tests.

Based on historical use and recent ordnance discoveries, all deactivated ranges with the "L" designation were used for small arms with the exception of the current L Range, which was used initially as an infiltration course and most recently as a grenade launcher training range. The current L Range, which is located on the western side of Greenway Road just north of the J-3 Range, has documented ordnance and explosive use.

Investigations in the study areas have included installation of more than 100 monitoring wells, collection and analyses of more than 4,000 soil and 3,500 groundwater samples, biweekly sampling of Snake Pond surface water, and monthly sampling of nearby residential and irrigation wells. Soil samples were analyzed using the standard analyte list plus dioxin/furans and PCNs. Groundwater was analyzed for the standard analyte list plus perchlorate. More recent analyses have focused on explosives, perchlorate, and SVOCs.

During the reporting period, an RRA was initiated at the J-2 and J-3 Ranges. The RRAs address perchlorate and explosives contamination in soil. Combined, the RRAs will remove and treat (or dispose of) approximately 7,900 cubic yards of soil. In addition, an RRA work plan was prepared to address groundwater contamination at the most downgradient portion of the J-3 Range Demolition Area groundwater plume.

Soil

Results indicate the presence of HMX in soil at various locations throughout the SE Ranges. At the J-3 Range, HMX and various propellants were identified at the following areas: the Melt/Pour facility, where melting of explosives and loading of munitions occurred; the northeast portion of the artillery range; a munitions detonation pit and burn area; and a drywell associated with an on-site workshop. At the J-1 Range, RDX was detected in ash samples collected from a former burn kettle and from mixed soil and debris from a steel-lined pit that contained discarded munitions. Explosive residues were present in the Ammunition Storage Magazine and the Melt/Pour building on the J-2 Range. PCNs were

also detected in many of the soil samples, as were low levels of dioxins and furans.

Soil sampling within the past year has been conducted primarily to refine the understanding of the extent of contamination. Results continue to confirm that perchlorate and explosives remain the principal COC. Soil sampling was also conducted to assist in identifying boundaries for the ongoing soil RRA.

Groundwater

Groundwater contaminants identified at the SE Ranges include RDX, HMX, TNT, and perchlorate. Four general regions of groundwater contamination have been identified at the SE Ranges (AMEC 2003a, 2003b). One plume is located downgradient of the northern end of the J-1 Range, one plume extends downgradient from the middle of the J-3 Range, and two plumes appear to emanate from the J-2 Range. While efforts completed during the past year have focused on defining the extent of the two J-2 Range plumes, progress has been made in providing better definition to the boundaries of the J-1 and J-3 Range plumes.

The J-1 Range plume is located immediately downgradient (northwest) of the J-1 Range 1,000- and 150-m berms, where perchlorate, RDX, HMX, and other miscellaneous explosives were detected in groundwater. RDX was detected at concentrations up to 150 μ g/L in this area. The highest HMX concentration observed in this area was 62 μ g/L, while perchlorate was detected at concentrations up to 37 μ g/L. Computer modeling of groundwater flow suggests that the contaminants reached the water table near the 1,000-m berm. Various activities known or reported to have occurred in the area could have provided a source for the detected contaminants. These include firing and detonation of munitions, cook-off tests, burning of excess munitions in the steel-lined pit and popper kettle, disposal by burning of lead azide on the range road, disposal of J-3 Range Melt/Pour wastewater, and burial of vehicles and open pails of various waste materials.

The J-3 Range plume is located from the center of the J-3 Range downgradient to Snake Pond, where RDX, perchlorate, and HMX to a lesser degree have been detected in groundwater. RDX was also detected in a water sample from a septic tank at the J-3 Range. The highest RDX concentration observed was 5.4 μ g/L, while the maximum HMX concentration was 18 μ g/L. Distribution in groundwater, groundwater modeling, and soil data suggest that multiple source areas may exist, including a detonation pit, the Melt/Pour building and drywell, and, although less likely, unidentified areas on the L or J-1 Ranges. Contaminants in groundwater are migrating south from the J-3 and L Ranges. Most of the contaminated groundwater discharges to or migrates beneath Snake Pond or is captured by the Installation Restoration Program (IRP) FS-12 groundwater extraction and treatment system. An RRA work plan has been developed to capture additional groundwater near the north end of Snake Pond, utilizing to the extent practical the FS-12 extraction system.

Two plumes have been identified at the J-2 Range. One, the northern plume, apparently originates within an area used for OB/OD activities at the northern

end of the range. Groundwater flow and plume orientation is towards the northeast. Perchlorate and RDX are the principal contaminants, with other explosives and dyes detected in near-source groundwater. The southern plume appears to have multiple small sources in the southern end of the range. Potential sources include former firing points, a melt/pour facility, and OB/OD activities. Contaminants include perchlorate and RDX, and, to a lesser degree, HMX. Groundwater flow and plume orientation are towards the east and northeast. The leading edge of the plume has not been defined.

Perchlorate has been detected at numerous widely distributed wells on the J-1, J-2, J-3, and L Ranges. The highest concentration (494 µg/L) was detected in a sample downgradient from the J-3 Range demolition area. PCNs and dioxin/furans have not been detected in groundwater.

Former A Range: Gravity Anti-Tank Range

The Former A Range is currently an inactive anti-tank artillery and rocket training range originally constructed in 1941 and used into the early 1960s. Tank targets were placed on specially designed rail cars and rolled on tracks, using gravity, downhill through two sets of switchbacks traversing a target area. Trainees would fire at these moving targets from gun positions located 2,400 ft from the target area. Records indicate that ordnance used during this period included 37-mm armor-piercing (AP) and HE rounds, 40-mm AP and HE rounds, 75-mm HE and shot rounds, 90-mm anti-aircraft rounds, and 3.5-inch practice rockets. Recent site inspections revealed the presence of 60- and 81-mm mortars and a single, inert 57-mm projectile. In the early 1960s, the range was converted for machine gun training. Records indicate that 0.50-caliber ball and tracer rounds were used at that time. Recent site inspections have revealed the use of 5.56- and 7.62-mm small-caliber ammunition as well.

Investigations of the Former A Range include soil testing and groundwater monitoring to determine if past training activities conducted there have had, or may potentially have, an adverse impact on groundwater. Groundwater monitoring in the vicinity of the Former A Range has been ongoing since February 1999. Other investigation activities included a ground-based EM-61 geophysical survey in the target area to search for subsurface ordnance and explosives. As part of these investigations, 38 blow-in-place (BIP) actions were performed on discovered ordnance items considered unsafe to move.

Soil

A total of 197 soil samples have been collected from within the target area, firing point, and target rollout area. The most frequently detected explosives were 2A-DNT and 4A-DNT. Both are considered transformation products of TNT, the primary filler constituent of 40-mm HE projectiles, which are known to have been fired at the Former A Range. RDX has also been detected in soils at this range; however, it was limited exclusively to post-BIP samples. Because none of the HE rounds destroyed during BIP activities at the Former A Range contained

RDX in their filler formulations, these results suggest that the presence of RDX, a primary constituent of BIP donor charges, is likely a result of the BIP process.

A suite of SVOCs, consisting mostly of polycyclic aromatic hydrocarbons (PAHs), was detected in soils collected from the target area and rollout area of the Former A Range. Most were found in samples collected from sediment deposition areas near the rail line. The link between the rail line and PAHs (typical of petroleum products) has not been confirmed. However, records suggest that maintenance of the rail line included the use of grease on the curved portions of the tracks for proper operation of the target cars. Two propellant-related SVOCs (N-nitrosodiphenylamine and di-n-butyl phthalate) were found in firing point soils. The presence of these compounds at the firing point, along with the detection of 2,4-DNT is consistent with past use of these compounds.

Among the several metals detected in soils collected from the Former A Range, lead and copper were frequently reported at concentrations greater than background. Because lead and copper are typical constituents of small arms projectiles, the presence of these metals in soil is presumed to be associated with past small arms training activities performed at the site. The maximum concentrations of lead and copper were 11,600 and 7,220 mg/kg, respectively.

Groundwater

Five monitoring wells were installed, in part, to evaluate groundwater conditions in the vicinity of the Former A Range. Monitoring wells were installed at three locations downgradient of the range and screened at depths selected to intercept groundwater originating beneath the target area. The two other monitoring wells were installed within the footprint of the target area. Of the five, only one location has shown explosives contamination associated with past training activities at the Former A Range. Trace concentrations of TNT (ranging from estimated values of 0.40 to 0.42 μ g/L), 2A-DNT, and 4A-DNT have been reported in this downgradient well. The detection limit for TNT in water is 0.2 μ g/L.

Geophysical Survey

A ground-based electromagnetic survey (EM-61) was conducted at the Former A Range to search for subsurface ordnance and ordnance disposal sites. Surveys were performed in four areas within the range target area, each representing a partially exposed, up-range hillside surface where ordnance was abundant. The survey results revealed numerous anomalies suggestive of possible subsurface ordnance items; subsurface inspections were performed at 102 of these locations. Eight of these anomalies were determined to be the result of disposal sites for expended practice rounds. Most of the 247 munitions recovered from these disposal sites were inert 3.5-inch rockets. Items other than 3.5-inch rockets discovered in these disposal pits included four inert 40-mm projectiles, one inert 37-mm projectile, one inert 75-mm projectile, and one inert 90-mm projectile. Of the remaining anomalies, 33 revealed ordnance items, of which 30

had to be destroyed in place to render them safe; the other three were crackedopen rounds. Most of the BIP items were 37- or 40-mm projectiles.

Phase IIB and Munition Survey Project Sites

The 12 sites identified in the original Phase IIB Field Sampling Plans were among several training areas, ranges, and other locations identified by the EPA to be investigated. The Phase IIB areas consist of waste oil sites (3), latrines (63), an ammunition supply point (1), cleared areas (12), general training sites (25), engineering training/demolition sites (5), and ranges (36). The ranges include small arms (22), machine gun (7), anti-tank (2), skeet (1), battle assault course (1), and grenade courts (3). Many of the Phase IIB sites are currently being investigated. Initial results suggest very limited detections of MEC compounds. In some cases, the U.S. Army/National Guard Bureau decided that limited additional sampling was necessary. The most surprising finding was the lack of explosives in soils at the former grenade courts. However, these grenade courts have not been used since WWII, and the grenades from this era likely contained TNT as the primary explosive. TNT is susceptible to transformation processes, which may account for its absence.

In addition to reconnaissance and soil sampling at these sites, geophysical surveys were performed at several sites. Although geophysical anomalies were found, upon subsequent excavation, no HE rounds were found. In most cases, metal debris, small arms ammunition, or inert projectiles were found, which would explain the anomalous geophysical signature, although occasionally nothing was found.

Twenty-five small arms ranges were evaluated as part of Phase IIB activities. The investigation consisted of review of historical activity, reconnaissance of the sites, and soil sampling. Four propellant-related SVOCs were detected at some of the ranges: 1,3-diethyl-1,3-diphenyl urea, di-n-butyl phthalate, N-nitrosodiphenylamine, and 2-nitrodiphenylamine. Five metals, antimony, barium, copper, lead, and zinc, were detected at concentrations sometimes exceeding established site background values.

Northwest Corner

The Northwest Corner consists of property on the northwest corner of Camp Edwards as well as the adjacent property beyond the base boundary between this part of the base and the Cape Cod Canal. Within Camp Edwards, the Northwest Corner encompasses portions of the B-9 and B-11 Training Areas, four gun positions (GP-12, GP-14, GP-16, and GP-19), and the L-3 Range, a former infantry squad and platoon combat firing range. Commercial and residential wells are located between the base boundary and the canal.

Investigation of the Northwest Corner was initially conducted as part of the comprehensive soil and groundwater characterization for the Gun and Mortar Firing Positions Operable Unit. With the detection of perchlorate in MW-66S at

GP-16 in August 2001, a focused investigation was initiated in the Northwest Corner specific to perchlorate. This included sampling of soil at GP-16 for perchlorate and sampling of off-site private wells located west and cross-gradient to GP-16.

In December 2002, perchlorate was detected in an off-site commercial well within the 4–18 µg/L range designated by EPA as the interim guidance level for perchlorate in drinking water. As a result, investigation of the Northwest Corner expanded to include plume delineation and source characterization. Monitoring well installation and sampling, identification and sampling of off-site private wells, and soil sampling were conducted in 2003 specifically to determine the extent of perchlorate in groundwater and soil in the Northwest Corner of Camp Edwards. The area of investigation included off-site areas located mainly on U.S. Army Corps of Engineers-managed property along the Cape Cod Canal. Explosives were also a potential concern based on the association of explosives with military training and specifically because of the detection of RDX in an off-site commercial well in an August 2002 sample.

Soil

Sampling was conducted at 41 locations to characterize perchlorate concentrations in shallow soil in the vicinity of Canal View Road at GP-16 and GP-19. In addition, soil samples were collected at 10 locations from an area containing fireworks debris along Canal View Road. Samples were collected both before and after the town of Bourne's annual Independence Day celebration to assess fireworks residual levels present in soil. Since 1997, fireworks for Bourne's celebration have been launched from an area located west of the MMR property boundary, 650 ft northwest of GP-19 and upwind of the Northwest Corner of Camp Edwards. In addition to soil sampling, paper fireworks debris from the 2003 display was collected from Canal View Road and analyzed to assess the possibility the debris represents a continuing source of perchlorate releases to soil.

Perchlorate concentrations in surficial soil along Canal View Road immediately after Bourne's 2003 fireworks display ranged from 4.5 to 7,560 μ g/kg. Samples collected prior to the event at the same locations showed traces or no detections of perchlorate. Soil analytical results from samples collected several weeks after the 2003 fireworks display indicate that perchlorate in soil in the Northwest Corner is distributed over a wide area at low concentrations ranging from an estimated value of 1.6 to 64 μ g/kg extending from Canal View Road just north of GP-19 northward to GP-16. Perchlorate concentrations in three soil samples collected two months after the fireworks display ranged from not detected to 18 μ g/kg. These concentrations were significantly lower than in soil samples collected two days after the display. Samples of paper fireworks debris were characterized by perchlorate concentrations ranging from 302 to 34,200 μ g/kg.

These data indicate that both particulates of perchlorate and pieces of the mortar shell paper from the fallout of fireworks debris containing perchlorate residues are a main source of perchlorate in the soil, with the paper fireworks debris continuing to be a source of perchlorate leaching to groundwater several months after the debris has been deposited. However, the majority of the perchlorate residue deposited from the fireworks display is rapidly dissolved and flushed through the soil. Trace concentrations of perchlorate in soil, observed in other training areas and gun positions where military training with pyrotechnics was historically conducted, suggest military pyrotechnic use is also a potential source. Low-levels of perchlorate found in soil (< 100 ppb) are believed to represent residues that are tied up in soil through sorptive processes and are no longer mobile.

Groundwater

Thirty-nine monitoring wells at 17 locations were installed within the Northwest Corner. In addition, 20 existing monitoring wells were sampled for perchlorate in conjunction with this investigation. Three commercial wells and six residential wells were sampled for perchlorate and explosives. The groundwater data indicate the presence of a shallow perchlorate plume approximately 4,000 ft wide and 5,000 ft long. Within this plume, perchlorate concentrations range from 0.36 to 19.3 μ g/L.

The highest concentrations of perchlorate are found at the water table beneath Canal View Road, just north of GP-19. This area coincides with the high perchlorate concentrations observed in soil and the presence of paper fireworks debris after the July fireworks display. In the upgradient portion of the plume, the highest concentrations of perchlorate were at the water table, with perchlorate present to a depth of 20–30 ft into the aquifer. With groundwater flow, the plume migrates lower in the aquifer, extending 20–50 ft below water table (bwt) at the southern downgradient end at the canal and 5–30 ft bwt at the northern downgradient end.

Source evaluation indicates that perchlorate in the shallow groundwater at the Northwest Corner probably originated from one or both of two sources: fireworks debris from the town of Bourne's historic July 4th celebrations launched from the Bourne Regional Technical School, and military use of pyrotechnics in Training Areas B-9 and B-11. The large areal extent and overall uniformity of the perchlorate plume suggest that the perchlorate was deposited from aerial dispersal over a large area. The distribution of the highest perchlorate concentrations in the middle of the plume at the water table suggests that the heaviest deposition of perchlorate occurred in the vicinity of Canal View Road north of GP-19, with lighter deposition upgradient and downgradient of the road and north along the road.

RDX has been detected sporadically in concentrations below 1 μ g/L in three wells located off the base, in both shallow and deep groundwater. RDX has been detected in two monitoring wells on the base in the Northwest Corner. In one well on the base, RDX was detected in profile samples from a depth of 40–130 ft bwt at concentrations of up to 5.5 μ g/L. Additional characterization is investigating the source of RDX in this well; modeling suggests that the deepest detections originated in the Central Impact Area. In an adjacent well, concentrations of RDX below 1 μ g/L were detected at the water table, which indicates a potential

source at the gun position (GP-19) immediately upgradient of the well. Explosives, however, are not a common contaminant found at the gun positions and are not a propellant constituent.

Overall Conclusions for MMR

Based on studies at Camp Edwards, explosive and propellant residues are deposited and accumulate on the soil surface as a result of normal military training activities. In the case of conditions at Camp Edwards, soil remediation activities may be necessary to remove the residues. Currently, soil concentrations of residues at Camp Edwards do not exceed regulatory guidelines.

Specifically, explosive residues were found in surface soils near indirect and direct-fire fixed targets used for a significant length of time. Propellant compounds were not typically found at artillery and mortar target areas, although perchlorate was found. The presence of perchlorate within the artillery and mortar impact area is a result of perchlorate used in the spotting charges for light infantry training rounds (LITR). The presence of a similar suite of compounds can be expected at most Army ranges. Similar to Camp Edwards, the explosive residues represent a distributed source covering a large geographic area. Higher contaminant concentrations are expected near the targets. Explosive and propellant residues are found at anti-tank targets, since the propellant is not entirely consumed before the rocket reaches the target.

At demolition areas, both explosive and propellant residues are found. Chunks of HE representing percent levels are found at the demolition areas. Perchlorate was found at Demo 1 but not at Demo 2. This dichotomy is related to burning of fireworks at Demo 1 but not at Demo 2. Residues can be expected at most Army demolition areas, with the distribution of compounds dependent on the type of munitions detonated. Since activities at demolition areas are concentrated in a small area, the residues are distributed over a small surface area. The concentrated activity will result in higher soil concentrations of residues than found at target areas.

Propellant residues are found at the anti-tank and artillery and mortar firing positions. In general, perchlorate was not found at the firing points, which is consistent with the absence of perchlorate in the propellant formulations used at Camp Edwards.

Because of favorable lithologic and geochemical conditions at Camp Edwards, some explosive residues and perchlorate have migrated to groundwater. For example, RDX, HMX, perchlorate, TNT, and the aDNTs have been found in groundwater in the vicinity of the artillery and mortar impact area, demolition areas, and munition testing ranges. These findings suggest that under the right conditions there is a good probability that some explosive residues can be expected in groundwater at other Army ranges. Plumes of explosive residues emanating from artillery and mortar impact areas are likely to be large spatially but have low concentrations. In contrast, plumes emanating from demolition areas are expected to be narrow, with the length dependent on the history of activities. Groundwater concentrations of explosive residues in demolition areas

will be higher than those at impact areas. Since RDX and TNT have relatively low health advisories, concentrations in groundwater are likely to exceed the regulatory guidelines.

In contrast, propellant residues have not been detected in groundwater at Camp Edwards coming from anti-tank or artillery and mortar firing points. These findings are consistent with the physical and chemical properties of the propellant compounds, which suggest that these compounds are not likely to be mobile in the environment. Since the site conditions at Camp Edwards represent an extreme environment favorable to contaminant mobility, the absence of propellants in groundwater at Camp Edwards suggests that propellants are not likely to be an issue at other Army ranges.

Overall, the findings at Camp Edwards suggest that general observations can be applied to ascertaining whether or not training activities have had an environmental impact at other Army ranges. Although residues of explosives and propellant can be expected at most Army ranges, the presence or absence in groundwater will require assessment on a case-by-case basis. Because of the number of variables affecting fate-and-transport behavior, a blanket statement about the presence or absence of groundwater contamination should not be made without collection of site-specific data.

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7 Assessment of the Long-Term Fate and Transport of Energetic Materials in the Vadose Zone Using Cracked 81-mm Mortars as a Source Term

This extended abstract will be published as a DRDC-Valcartier Technical Report in autumn 2005.

Introduction

Knowing the long-term fate and transport of energetic materials through the vadose zone is important for understanding how explosives ultimately reach the water table. If contaminants in the vadose zone are immobile, remediation or removal becomes fairly straightforward. However, once a contaminant enters the groundwater, clean-up becomes much more challenging and costly. Therefore, the mechanisms of transport through the vadose zone are key to the development of remediation efforts. This study will seek to better define the parameters influencing the fate and transport of energetic materials in the vadose zone using cracked munitions as a source term. The goal of this work is to provide a link between laboratory-scale studies and range characterization studies. Laboratory work tends to be theoretical. Many practical questions are left unanswered using this approach: How much explosive will dissolve in the rain after a low-order detonation? What is the rate of the dissolution? How much of the dissolved explosive from a cracked munition will sorb on the soil? How quickly will this dissolved explosive reach the water table? This experiment will use an engineering approach to try to reproduce what is being seen in the field and will try to answer some of these pragmatic questions.

The explosives contained in the munitions have potentially negative impacts on the environment. The build-up of explosives residues in the soil may contaminate groundwater (Jenkins et al. 2001). Such a situation has been encountered at the Massachusetts Military Reservation (MMR) in the United States, where the Environmental Protection Agency (EPA) suspended training because low RDX

concentrations were found in the groundwater (EPA 2000). RDX and other high explosives have been identified as potential carcinogens (ATSDR 1996). At MMR, RDX is thought to originate from leaking UXOs, low-order detonations, residues of past munitions disposal, or accumulated residues over the years. The contamination caused by functioning munitions and munitions blown-in-place has been studied by various research teams in field conditions (Jenkins et al. 2000, Hewitt et al. 2003, Lewis et al. 2003, Brochu et al. 2004, Dubé et al. 2004). However, no work has been performed on leaching of explosives from UXOs or cracked munitions.

The leaching study will be conducted for a minimum of 12 months starting in September 2004; therefore, these results are not currently available. The experimental production of the cracked shells will be emphasized in this abstract, as this phase of work was successfully completed in January 2004. However, the experimental plan of the hydrogeological leaching study will be presented as well. For clarity, the production of the cracked shells will be referred to as Phase I, and the hydrogeological study will be referred to as Phase II.

The objective of Phase I of this study was to create the UXOs, which would act as source terms for Phase II. One key requirement was that the steel shell of the munitions be breached, exposing the explosives inside. This meant that the explosives could not detonate or burn completely and that a large fraction of the explosive must remain in or around the broken shell. An unexpected result of the experimental setup of Phase I was the identification of a new type of UXO, which we have named the cracked shell. Cracked shells were subsequently used as the source term during Phase II of the study.

The objective of Phase II is to determine the rate at which explosives are mobilized from cracked shells through the vadose zone and to the groundwater under conditions typical of local soil and groundwater. Data will be compared to data generated with an inert tracer and to unconfined granulated Composition B.

Phase I: Generation of Cracked 81-mm Mortars

Phase I - Experimental

Materials. The Canadian 81-mm C70A1 mortar was used for all trials. The choice of the 81-mm offered several advantages. First, it is used both in Canada and the United States. Second, the Composition B explosive fill contained in the projectile is the same in both countries and is widely used in other munitions. Third, the shell was an ideal size to fit in the columns during Phase II. The 81-mm mortar is filled with 0.9 kg of Composition B (59.5 percent RDX, 39.5 percent TNT, and 1 percent wax) (Canadian National Defence 2000). Prior to detonation, the propellant was removed because it is completely consumed during launch; thus, it would not be present in either UXOs or normally detonating rounds. The fuze was also removed for safety purposes. The fuze was not replaced with an inert fuse for most tests, to increase the likelihood of obtaining cracked shells. An inert plug was used for one test only.

The trials chosen for use during Phase II were performed on snow, with the detonation residue collected by removing a 2- to 5-cm-thick layer of snow and storing it in large plastic bags. The cracked shell itself was also collected. The bags of snow were later freeze-dried in the laboratory to separate the residue from the snow without exposing the residue to liquid water, eliminating the possibility of losses due to dissolution. By holding the pressure below the triple point, water vapor can be drawn off the solid ice. This process is commercially used to preserve food products.

Method 1. C4 Attack. Composition C4 in sub-critical quantities, in blocks, or in linear shaped charges was applied to the outside of the shell to simulate the blow-in-place of UXOs by ammunition technicians. The shaped charges were Canadian military issues (Mk 7 series) (Canadian National Defence 1996) hand-filled with C4. Method 1 represents what would happen if the wrong amount of explosives or the wrong type of charge were used in range clearance operations. This method could also represent the attack of munitions by a strong non-fragmentary blast very close to the item. Finally, by placing C4 near the nose of the round, the effect of a strong impact by a non-functioning round with a hard target (e.g., a rock, another round, a target) could be simulated.

The C4 was applied in various amounts and at various positions on the outside of the mortar round. Various sizes of shaped charges were used, with different standoff distances. Table 7-1 summarizes the experimental conditions used. Figure 7-1 shows several different configurations for Method 1.

Twenty-three trials of Method 1 were performed in January 2004 at the DRDC-Valcartier trial site on the Canadian Force Base Valcartier. The early trials were done on a thick metal plate until the right conditions were found to crack shells. The successful ones were then repeated on snow to ensure a maximum recuperation of the explosives and a minimum contamination by soil. This approach was taken to maximize the number of trials. Preparation of the snow-pack was very time consuming, and we only had two weeks to complete our work. The surface area of the snowpack was roughly 3 m × 3 m. A large metal plate was buried in the middle of the snowpack under approximately 30 cm of fresh packed snow.

PCB 113B52 pressure gauges were placed at 10 m from the detonation point to measure the overpressure generated by the events. The overpressure data suggest whether the round detonated completely or a low-order detonation was produced. The gauges were triggered by an ionization pin placed in the C4.

Method 2: Fragment Attack. The second method consisted of detonating a mortar shell next to another similar round, in order to simulate the attack of a UXO by another incoming round that functions. It is similar, in many ways, to a sympathetic detonation trial (NATO 2002). A booster charge of 40 g of C4 was employed in all trials. Two 81-mm mortar projectiles (A and B) were used for each trial. Projectile A was the intentionally detonated projectile, which simulated a round that functions normally (Figure 7-2). Projectile B served as a UXO lying on the ground in the vicinity of the point of impact of an incoming round (Projectile A).

Table 7-1 Experimental Conditions Used in Method 1				
Trial #	Type of Attack	Position	Amount of C-4 used (g)	
1	Mk 7 Mod 1 shaped charge	Longitudinal, 0 stand-off	15.1	
2	Mk 7 Mod 1 shaped charge + C4 ball	Longitudinal, 0 stand-off	16.3 + 5.7*	
3	Mk 7 Mod 2 shaped charge + C4 ball	Longitudinal, 0.5-cm stand-off	15.4 + 7.7*	
4	Mk 7 Mod 3 shaped charge + C4 ball	Longitudinal, 0 stand-off	24.7 + 5.0*	
5	Mk 7 Mod 2 shaped charge + C4 ball	Perpendicular, 2.9-cm stand-off	16.0 + 7.0*	
6	Mk 7 Mod 4 shaped charge cut in half	Perpendicular, 1.5-cm stand-off	27.1 + 6.0*	
7	Mk 7 Mod 8 shaped charge cut in half	Perpendicular, 9.5-cm stand-off	71.0	
8	C4 ball	In fuze well	20.0	
9	C4 ball	In fuze well, 2.5 cm stand-off	10.0	
10	C4 block	Outside, at the nose	72.3	
11	C4 block	Outside, at the nose	72.0	
12	C4 block	Outside, at the nose	72.0	
13	C4 block	Outside, at the nose + plug fuze	70.2	
14	C4 block	Outside, at the nose	72.1	
15	C4 block	Outside, at the nose	90.0	
16	C4 block	Outside, at the nose	80.0	
17	C4 hemisphere	Outside, at the nose	80.0	
18	C4 hemisphere	Outside, at the nose	80.0	
19	C4 hemisphere on cracked shell	Outside, at the nose	80.0	
20	C4 hemisphere	Outside, at the nose	80.0	
21	C4 hemisphere on cracked shell	Outside, at the nose	80.0	
22	C4 hemisphere on cracked shelf	Outside, at the nose	63.2	
23	C4 hemisphere on cracked shell	Outside, at the nose	64.0	
* Amoun	ts refer to mass of C4 in shaped charge + mass	of C4 ball required to seat detonator on sl	haped charge	

The two 81-mm mortars were placed one over the other (Figure 7-3); one was laid on a metal plate, and the other was suspended by chains. The first objective was to determine the distance at which the reaction would change from a detonation of Projectile B to the production of a cracked shell. The second objective was to determine the distance at which Projectile B would remain intact. The third objective was to determine the effects of placement of Projectile B in the ground, on snow, and underwater.

To maximize the number of fragments from Projectile A hitting Projectile B and to simulate the worst-case scenario, the fragmentation pattern of the 81-mm mortar was analyzed¹. The zone for a maximum number of fragments was determined to be between 85° and 105°, where 0° was at the nose of the projectile and 180° was at the tail end. Thus, Projectile A was placed parallel to B, with an angle of 95° between the driving band (roughly the larger diameter) and the point of impact on Projectile B (see Figure 7-2). The point of impact selected for Projectile B was 5.5 cm from the projectile nose. At this spot, the wall of Projectile B was the thickest. This spot appeared to be the ideal place in order to

¹ Personal Communication, fragmentary pattern of 81-mm mortar, C. Fortier, DRDC-Valcartier, Sept 2004.

be able to crack the projectile. Table 7-2 shows the distances between the projectiles for the various experiments.

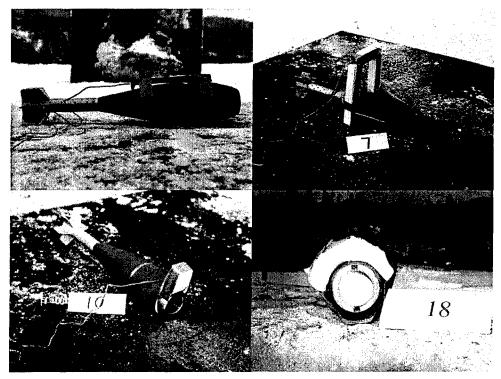


Figure 7-1. Configurations used in Method 1. Top left: small shaped charge longitudinal, minimal standoff. Top right: larger shaped charge, large standoff. Bottom left: Small block of C4 at the nose. Bottom right: Hemispherical configuration of C4 at the nose

For a small number of trials, the conditions were changed to reflect situations that are found in the field. For one experiment, the round was placed on fresh snow instead of on the metal plate. In this trial, the detonation residue was collected as in Method 1 and stored for used in Phase 2. For other trials, Projectile B was covered by various depths of sand, with or without an angle of entry. Finally, one trial was performed in which the round was immersed in water, a situation that was reported by ammunition technicians as common in some of our training ranges where UXOs are found in small ponds. PCB 113B52 pressure gauges were placed at 10 m from the detonation to measure the overpressure generated by the events.

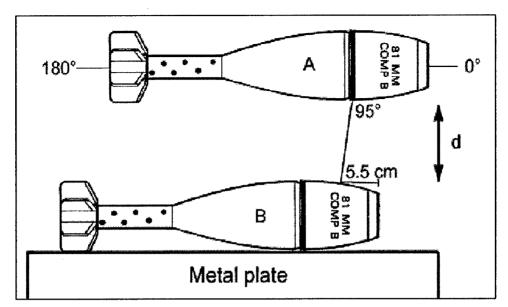


Figure 7-2. Experimental set-up for Method 2

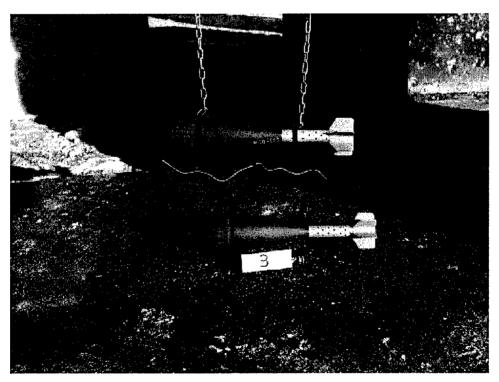


Figure 7-3. Picture of the experimental set-up for Method 2

1	Table 7-2 Experimental Conditions Used in Method 2				
Trial #	Distance between Projectiles (cm)	Material Underneath Projectile B	Material Above Projectile B		
1	0	Metal plate	-		
2	20	Metal plate	-		
3	15	Metal plate	-		
4	10	Metal plate	-		
5	13	Metal plate	-		
6	15	Metal plate	-		
7	15	Metal plate	-		
8	25	Metal plate	-		
9	45	Metal plate	-		
10	100	Metal plate	-		
11	157	Metal plate	-		
12	15	Snow	-		
13	15	Sand	Sand 2.5 cm		
14	15	Sand	Sand flush with top		
15	15	Sand	Sand at mid-depth		
16	15	Sand	Sand (proj. planted at 45°)		
17	15	Sand	Water 5 cm		

Phase I - Results

Method 1. C4 Attack. In general, the shaped charges did not generate cracked shells (Table 7-3). The shaped charges were not powerful enough to penetrate the metal casing of the shell, and they failed to significantly expose the Composition B filler. An example of such an event is shown in Figure 7-4. Only the larger shaped charge (Trial #7) pierced the mortar round significantly. This was not deemed acceptable for the subsequent hydrogeological leaching studies with the shells, since an insufficient amount of Composition B was exposed. C4 placed on the nose of the projectile, however, proved very successful. The C4 removed the metal in the fuse cavity and exposed the Composition B contained inside of the mortar rounds (Figure 7-5). This was considered acceptable, and some of the trials were repeated on clean snow. These projectiles and the detonation residue surrounding them were kept for the leaching study. The upper limit of this method was determined in Trial #15 when the projectile detonated with a larger amount of C4 (90 g). The number of detonations was low (only two). No low-order events resulted in large amounts of explosives being scattered around the site. Creating cracked shells was surprisingly easy with 81-mm mortars, an indication that this may also occur in the field during firings or range clearances.

	Table 7-3 Results for Method 1			
Trial	Resulting Condition of Projectile B			
1	No effect			
2	Groove blasted into projectile casing			
3	Thick groove blasted into projectile casing			
4	Long thick groove blasted into projectile casing			
5	Thin groove blasted into projectile casing			
6	Thick groove blasted into projectile casing			
7	Thick groove, casing opened, Comp. B exposed			
8	Detonation			
9	Exposed Comp. B in the fuze well			
10	Cracked, exposed Comp. B			
11	Cracked, exposed Comp. B			
12	Cracked, exposed Comp. B			
13	Partial Crack at the nose and plug fuze			
14	Cracked, exposed Comp. B			
15	Detonation			
16	Cracked, exposed Comp. B			
17	Cracked, exposed Comp. B			
18	Cracked, exposed Comp. B			
19	Cracked, exposed Comp. B			
20	Cracked, exposed Comp. B			
21	Cracked, exposed Comp. B			
22	Cracked, exposed Comp. B			
23	Cracked, exposed Comp. B			

Method 2: Fragment Attack. The attack by fragments seemed to be a very efficient way of obtaining cracked shells and exposing explosives, and it was more effective than Method 1. For the trials done on the metal plates, when the distance between the projectiles was smaller than 15 cm, a sympathetic detonation occurred and both rounds were destroyed (Table 7-4). Above that distance, even at distances up to 157 cm (which was the maximum for our set-up), the projectiles were damaged and the explosives were exposed. At such long distances, the number of fragments hitting Projectile B was much lower, resulting in less damage. However, those fragments that hit were able to penetrate the casing. This is an indication that, in an impact area with many UXOs, the likelihood of a UXO being hit by a fragment is rather high, given that incoming rounds potentially generate thousands of fragments. Examples of the cracked projectiles obtained at short and long distances between the rounds are shown in Figures 7-6 and 7-7.

Results of the trial done on snow (# 12) did not produce significantly different results. The sand, at a thickness of 2.5 cm, protected the projectile (# 13) from the fragments and acted as confinement in the case of Trial # 14, when a low-order detonation was observed. Water did not protect the projectile from the fragments and also acted as confinement to cause a low-order detonation. In both

cases of low-order reactions, the likelihood of getting this result in the impact area seems quite high.



Figure 7-4. Effect of a shaped charge, showing groove blasted into projectile casing (Trial #2)



Figure 7-5. Cracked shell produced by C4 on the nose (Trial # 22)

	e 7-4 ults for Method 2
Trial	Resulting Condition of Projectile B
1	Detonation
2	Cracked and explosives scattered
3	Cracked and explosives scattered
4	Detonation
5	Detonation
6	Cracked and explosives scattered
7	Cracked and explosives scattered
8	Cracked and explosives scattered
9	Cracked and explosives scattered
10	Pierced and bare explosives exposed
11	Pierced and bare explosives exposed
12	Cracked and explosives scattered
13	Lost its shape but not pierced
14	Low order detonation and explosives scattered
15	Cracked and explosives scattered
16	Cracked and explosives scattered (Only the exposed part and 3 cm of the buried part)
17	Low order detonation and explosives scattered



Figure 7-6. Projectile attacked by fragments at a short distance (Trial #6)



Figure 7-7. Projectile attacked by fragments at a long distance (Trial # 11)

Phase 1 - Conclusion

Cracked 81-mm mortars were obtained using two methods. Remnants of these are now available for the study on the transport of explosives during Phase II. The use of a small amount of C4 on the nose of the munitions was an effective means of producing cracked shells during Method 1 attacks. However, superior results were obtained by fragmentary attacks during Method 2. Shrapnel from a donor shell easily produced cracked shells and low-order detonations at standoff distances greater than 15 cm. Both methods produced reproducible cracked shells. The 81 mm mortars were easy to break open without causing detonation.

The initial hypothesis was that a sympathetic reaction caused by the pressure from an incoming round would be the best way to generate cracked shells and that fragments would tend to detonated rounds upon impact. The study demonstrated instead that fragments are more efficient than pressure at creating the cracked shells found in real firing situations.

The results suggest that cracked shells could be the cause of significant contamination by explosives on training ranges. If true, the frequency and methods of training and range clearance may require modification, particularly at fixed firing positions used for many years, which tend to create a high UXO density at the point of impact.

Phase II – Hydrogeological Leaching Trials

Phase II - Experimental

Materials. The hydrogeological leaching aspect of this study has been initiated in six separate soil columns, 60 cm in diameter and 75 cm deep (Figure 7-8). These columns are located in a dedicated laboratory refrigerated to 8 degrees Centigrade. The soil in the columns was obtained from a firing range on Canadian Force Base-Valcartier near Quebec City and is a silty sand. Granulometry is scheduled to determine the precise composition of the soil. Qualitatively, it closely resembles the sandy soil commonly found on several other Canadian Forces bases such as Canadian Forces Base (CFB) Shilo, Wainwright, Suffield and Cold Lake. The soil was thoroughly mixed to eliminate any heterogeneities. This was followed by screening to remove any stones larger than 0.7 cm in diameter.

The columns were manufactured of ¼-in.-thick 304 stainless steel lined with Teflon (Figure 7-8). This heavy gauge material was required because of the stresses placed on the column during compaction of the soil. All parts were rinsed with acetone prior to addition of the soil. The soil was added to the column in uniform 1700-g layers, which corresponded to a 1-cm compacted thickness. It was then compacted thoroughly with the jack drill, and the surface was scarified to provide a hydraulic connection between the sand layers. This was repeated until the sand level was 75 cm deep. Care was taken to produce homogenous conditions in all six columns. The columns are each fitted with an automated spray system, which simulates the annual water infiltration cycle for the Quebec City region.

The columns were designed and scaled to reproduce vadose zone conditions. Because of the size of the cracked shells, the columns could not be smaller than 60 cm in diameter. With large columns such as these, the outflow must be collected from multiple nozzles at the bottom of the column. It was considered ideal to use seven nozzles, as this number was sufficient to provide a uniform outflow from the bottom of the column yet were not so numerous as to structurally weaken the bottom. With the seven nozzles spaced equally around the bottom, the distance between the nozzles is 22 cm. This means a drop of water, upon reaching the bottom of the column, may have to travel up to 11 cm horizontally before it reaches a nozzle. Because vadose zone flow is uniquely exclusively vertical, it was necessary to maximize the vertical flow/horizontal flow ratio. A column length of 75 cm was deemed sufficient to maximize this ratio.

Instrumentation. The columns were each instrumented using time domain reflectometers (TDRs) connected to a Campbell datalogger (model CR-10, Campbell Scientific Canada, Edmonton, Alberta) via three multiplexers. This system allows the real-time measurement of the volumetric water content (θ) of the soil and has the advantage of being nondestructive. Measurements can be taken without disturbing the system. The TDR probes were coated in Teflon and inserted through the column wall via drilled holes. The TDRs were installed during the sand compaction and will remain inside the columns for the duration of the experiment.

Hydraulic conductivity. Following the sand compaction, the hydraulic conductivity was determined for each column using a Guelph permeameter (Figure 7-9). The infiltration rate was measured at 3–5 different tensions varying from -250 to -10 mm. A porous plate was used in conjunction with the Guelph permeameter, and this plate created a hydraulic link with the surface of the soil. The rate of descent of the water level in the main reservoir was the information used to calculate the hydraulic conductivity.

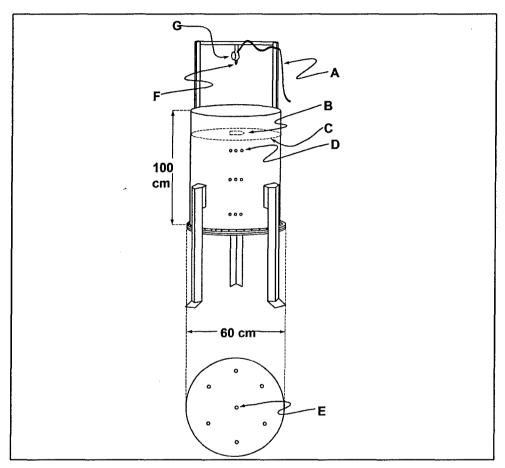


Figure 7-8. Schematic of column. A is the water feed line. B is the cracked-shell source term. C represents the surface of the soil. Ds are the access holes for the time domain reflectometers (TDR). E is a leachate outflow nozzle. F is the infiltration spray nozzle, and G is the electric valve controlling flow

Spraying System. The spraying system to infiltrate the columns was selected to produce uniform spray coverage over the surface of the column (a diameter of 60 cm) at a very low flow rate. The spray nozzle that best fit our needs was the UniJet model TG 0.3, which at 30 psi produces 0.197 L per minute. In the Quebec City area, there are only two periods of significant water infiltration. The first and most significant is in the springtime, when the snowpack melts, and the second is in the autumn, with two months of heavy rainfall. Other infiltration events during the year are not significant compared to these two and will not be considered. The spray cycle for springtime infiltration is 1.5 minutes per hour from 9 am to 4 pm (the period of the day above 0°C) for 30 days (the month of

April). During the autumn infiltration period, the spray cycle is 6.6 seconds/hour, 24 hours per day for 61 days (October–November). Such short timeframes required substantial control over the spray system. An electric valve was installed between the water feed line and the spray nozzle. This valve was controlled by the CR-10.

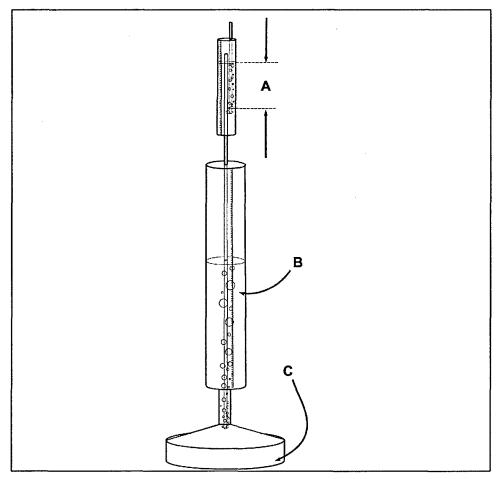


Figure 7-9. Guelph permeameter. A shows the tension measurement, B shows the main reservoir, and C shows the porous plate

The electric valve on each of the six columns is connected to its own dedicated 20-L water reservoir (Figure 7-10). The six reservoirs were constructed of schedule 80 PVC and were each equipped with a fill valve, pressure hose inlet, outflow valve connected to the water feed line, and transparent scale tube to monitor the water level. The pressure hoses on all six reservoirs were connected to a single manifold, which distributed the pressurized air equally. Therefore, even if there was an unexpected variation in air pressure, it would change equally for each of the columns, and no difference in water volume sprayed should be encountered. As well, all water feed lines were cut the same length to prevent variations in resistance caused by different lengths of tubing. Table 7-5 shows the experimentally measured flow rates from each of the spray nozzles.

The water used for infiltration is simulated rainwater consisting of distilled water with the pH adjusted to 4.7, which is the annual mean pH for rain in the

Quebec City region. The pH adjustment was accomplished with concentrated HCl.

Table 7-5 Flow Rates	s of Spray	Nozzles				
		Time to fill g	raduated cylir	nder to volum	e indicated (s	s)
Volume (mL)	Column A	Column B	Column C	Column D	Column E	Column F
50	16	16	16	15	17	17
70	23	22	21	21	23	22
90	28	28	27	27	29	28
110	34	35	33	33	36	34
130	40	40	39	39	42	40
150	45	47	45	45	49	47
250	75	76	76	76	80	75

Experimental Design. Each column will be monitored continuously for the volumetric water content using the TDRs. Leachate flowing from the column through the outflow nozzles will be collected in graduated cylinders and the volumes tabulated. Five hundred milliliters of water will be drawn from the outflow for chemical analysis on a regular basis, dictated by the rate of leachate outflow.

The detonation residue used in the columns will be a composite of residue from five crack-shell trials. This is necessary to have enough homogenous residue to split between four columns and still retain enough for laboratory analyses to allow complete characterization of the residue. Twenty-five grams of the composite detonation residue will be used in each of the four columns.

Table 7-6 shows the source terms for each column. The cracked shells used as source terms were those obtained in Trials 12 and 15 of Method 2, fragment attack.

Phase II - Discussion

The fate and transport parameters for four energetic material source terms will be produced. The detonation residues are hypothesized to have the shortest breakthrough time because they consist of very fine particles with an extremely high surface area. High surface area increases the rate of dissolution of the energetic materials as compared to source terms with less surface area (such as in the cracked shells). However, the mass of the residue is very small compared to the 500–750g of Composition B remaining in the cracked shells. Despite the large mass of the cracked shells, the Composition B is in large chunks. One of the questions that these trials should help answer is which source is more significant: the detonation residue or the cracked shells themselves? Depending on the answer, approaches to remediation would be very different.

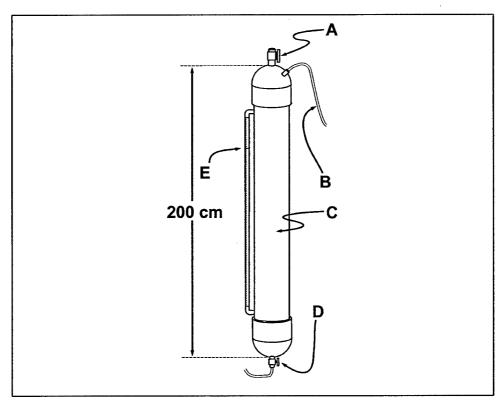


Figure 7-10. Pressurized water reservoir. A is the fill valve, B is the pressure hose inlet, C is the schedule 80 PVC pipe, D is the outflow valve connected to the water feed line, and E is a transparent scale tube to monitor the water level

li e	Table 7-6 Source Terms				
Column	Source Term				
Α	Potassium Bromide (Inert Tracer)				
В	25 g Granulated Comp B (Control)				
С	25 g Detonation residue (Soot, Comp B particles, metal particles)				
D	25 g Detonation residue (Soot, Comp B particles, metal particles)				
Е	Cracked shell and 25 g detonation residue				
F	Cracked shell				

Infiltration data for the Quebec City region will be used for the water application protocol (Mailloux 2002). In Quebec, no infiltration occurs between December and March, as the ground is frozen. Statistically, no infiltration takes place from June to September because of the dry summer months. Therefore, as long as a year may be required to achieve breakthrough of the energetic materials in the outflow collected below the columns if realistic flow rates are applied. Therefore, the infiltration cycle will be accelerated to obtain results more quickly. An obvious disadvantage to accelerating the cycle is the risk of producing unrealistic conditions that may negatively affect the reliability of the fate and transport parameters. A compromise was achieved by shortening the two dry cycles between infiltration seasons. The dry season is postulated to contribute little to the fate and transport of contaminants in the vadose zone, and the vast

majority of transport activity is expected to occur during infiltration events. The infiltration cycle will, therefore, be doubled with two years of activity occurring in one year. This is achieved not by increasing the rate of infiltration, i.e., doubling the rate of water sprayed on the column, but halving the dry periods between infiltration events. The reduced experimental duration will also reduce the likelihood of fungal growth in the column, a problem observed in longer-duration studies.¹

Phase 2 was started on 17 September 2004 with the initial infiltration of water to bring the water content in the columns up to the field capacity. The volumetric water content in the columns was uniform as measured by the TDRs, with the top 25 cm in each column registering around 17 percent, the middle 25 cm 27 percent, and the bottom 25 cm around 36 percent. Breakthrough of energetic materials occurred by 22 September 2004. Analysis of the raw data is ongoing, and a complete report will be available in autumn 2005.

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8 Explosives Residues
Resulting from Blow-inPlace Detonation of
Composition-B-Filled
Fuzed 155-mm HighExplosive Artillery
Projectiles

Introduction

Range characterization is a critical component to the sustained operation of active military training ranges. For proper characterization to occur, baseline data on residues remaining after detonation of ordnance are required. These data include residues derived from both live-fire and blow-in-place detonations. This section covers work conducted during March 2004 at Eagle River Flats, an active Army impact range on Fort Richardson, Alaska. Residues resulting from the blow-in-place (BIP) detonation of seven 155-mm howitzer rounds were collected and analyzed for composition and mass deposition. Data from this test will fill a gap in the current range sustainment database and will be used for current range management.

Objective

The objective of this test was to determine the identities and masses of explosives residues following the detonation of Composition B-filled 155-mm howitzer high-explosive projectiles. The rounds were fuzed and detonated with donor charges of C4 explosive to simulate blow-in-place disposal of unexploded ordnance on active military training ranges.

Field Site

The field tests were conducted at the U.S. Army Alaska (USARAK) Eagle River Flats impact area (ERF) on Fort Richardson in Anchorage, Alaska. All tests were conducted on snow-covered ice. Rounds were placed on 0.5-m-thick ice blocks to ensure that the blast and shrapnel from the detonating round would not penetrate the 25- to 75-cm ice cover to the ground and thereby contaminate the plume with residues present in underlying sediments (Figure 8-1).



Figure 8-1. Detonation test set-up at Eagle River Flats, AK

All rounds were detonated within seconds of each other, ensuring consistency of meteorological conditions during testing. Access to the detonation area was via an ice road. Access to the detonation plumes was via a snowmobile path. Collected samples were processed at a nearby laboratory on post prior to shipment for chromatographic analysis to the analytical chemistry laboratory at the Cold Regions Research and Engineering Laboratory (CRREL) in Hanover, NH.

Methods

Seven M107 155-mm HE projectiles, each containing 7,000 g of Composition B (2,700 g of TNT, 4,200 g RDX) were requisitioned for the test. Each projectile was fitted with an M739 point-detonating fuze for testing (21 g RDX). The fully assembled rounds are representative of undetonated rounds (duds) found in artillery impact areas.

Prior to placement of the projectiles at the test site, access routes were cleared by a UXO contractor, and ice and snow thickness measurements were taken. An ice road was plowed along the cleared lane to the test location. Detonation points were then set up along a line intersecting the ice road at 50-m intervals. An access path was demarcated 3–5 m from the designated detonation points (Figure 8-2). This path was packed using snowmobiles. Ice blocks $(1 \times 0.6 \times 0.6 \text{ m})$ cut from a nearby lake were placed at each detonation point.

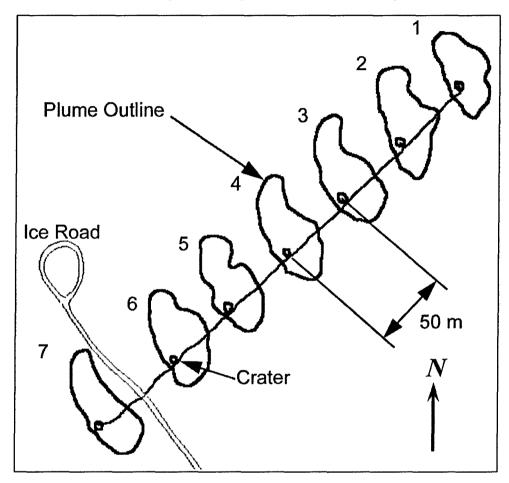


Figure 8-2. Detonation layout and plumes from test

The projectiles were placed on the ice blocks, and a 570-g block of C4 was attached near the nose as a donor charge following the standard blow-in-place practice used by the military. A blasting cap was used to initiate each block of C4. The caps were connected to a central initiator using detonation cord and time fuze. The detonation of the rounds was slightly staggered to reduce the noise impulse. A list of munitions used, including lot and DODIC numbers, is given in Table 8-1.

Table 8-1 **Munitions and Explosives Data**

NSN	DODIC	Nomenclature	Lot Number	Qty. Drawn
1320012574222	D544	Projectile, 155MM, M107, HE, W/O Fuze	IOP03E100-011	7
1390010809447	N340	Fuze, Point detonating, M739	MA-84B007-013	7
1375014151232	ML47	Cap: Blasting Non-electric, 30 Foot, M11	EBW97K060- 008	8
1375014151231	MN03	Cap, Blasting, Non-electric, M13	ENB00M002- 007	12
1375014151233	MN06	Cap, Blasting, Non-electric delay, M14	SHK98D001-001	5
1375001809356	M456	Cord, Detonating, Pentaerythritol tetranitrate	EBG03A002-015	1000 ft
			ENB83H001-027	6000 ft
1375014151235	MN08	Igniter, Time blasting fuse with shock, M81	LNO98E001-003	9
1375007247040	M023	Charge, Demolition, Block, Comp C4, M112	MA-97A003- 007A	7

Notes: Drawn from Fort Richardson Ammo Supply Point 15 MAR 04 Data from DA Form 581 - Request for Issue and Turn-in of Ammunition Some munitions quantities used in subsequent tests are not covered in this report.

Following the detonation of the projectiles, the plumes were visually demarcated by walking along the edge of the soot, and the perimeter of each plume was recorded using a Trimble Pro-XRS GPS system (sub-meter resolution, Trimble Navigation, Limited, Sunnyvale, CA). Snow surface samples of the residues were collected over the whole plume to a depth of 2 cm (Jenkins et al. 2002). Sampling was done using multi-increment sampling methods developed during prior tests at ERF and Donnelly Training Area in Alaska (Walsh, M. R. et al. 2004, Walsh, M. E. et al. in prep). Two methods were employed: a large-increment (about 100 increments) sample was collected using a 10- × 10-cm hand scoop and a multi-increment (40 increments) sample was collected using a 15- × 15-cm scoop (Figure 8-3). Both methods resulted in the collection of approximately 1 m² of surface residues per sample. The large-increment samples included increments from within the crater; the multi-increment samples did not. Individual crater samples were taken using 20- x 20-cm scoops. Additional soot samples were collected from several craters for further analysis by the Defence Research and Development Canada (DRDC-Valcartier) by a team of Canadian researchers assisting with the tests. All samples were collected within three hours. The temperature was -7°C with a light wind (0-3 m/s) out of the southwest under partially cloudy skies at the time of detonation.



Figure 8-3. Sampling residues

Field quality assurance (QA) procedures conducted during sampling included duplicate and triplicate sampling, adjacent sampling, subsurface sampling (below sampled points), and sampling outside the demarcated plume. The QA procedures developed for these tests are presented in detail in M. R. Walsh et al. (in prep). All QA procedures were conducted using multi-increment sampling. Adjacent sampling was conducted on two plumes using the multi-increment procedure to determine sampling repeatability through close-proximity sampling. Subsurface sampling beneath one of the multi-increment samples was done in each of the two plumes to determine if any residues resided below the 2-cm surface layer being sampled. Duplicate and triplicate samples using the large-increment procedure were taken on all plumes to determine repeatability of the samples, and sampling outside the plume was conducted at each site to determine if the plume demarcation was accurate and if any residues were being missed.

Processing of the melted samples at Fort Richardson consisted of filtering and concentrating the filtrate. Samples were melted and passed through a vacuum filtration unit containing a glass fiber filter (Whatman GF/A 90-mm). The filters were stored in refrigerated 4-oz (about 118 cm³) amber glass jars. A 500-mL aliquot of the filtrate was taken and pre-concentrated using solid phase extraction (SPE) with a Porapak RDX cartridge and elution with acetonitrile to 100:1 in 7-mL amber vials. The concentrated filtrate was then split into 3.7- and 1.3-mL fractions. The larger volume was sent for analysis to the CRREL analytical laboratory along with the filters, and the smaller vial was retained as a backup in Alaska.

Two QA procedures were conducted in the Alaska field laboratory. Distilled water was run through the filtering apparatus and processed as a field sample

using SPE for further analysis on the chromatographic instruments to determine if residual contamination remained on the processing equipment between samples. Duplicate samples were also taken of the filtrate and processed by SPE for analysis.

Soot-laden filters and concentrated SPE filtrate fractions were analyzed at the CRREL laboratory in Hanover, NH. Filtrate samples were prepared following EPA Method 8330 (EPA 1994). Analyses were conducted using gas chromatography with electron-capture detection (GC-ECD), reversed-phase high-performance liquid chromatography (RP-HPLC), or both methods. The filters were similarly analyzed after extraction with acetonitrile on a shaker table (Hewitt et al. 2003). QA procedures included the running of analyte standards and deionized water blanks.

Results

Detonation tests for the seven projectiles were conducted over two days: one day for site preparation and one day for detonation of the projectiles and the sample collection. A total of 42 samples consisting of 3,239 increments were taken from the seven plumes. On-site processing, including SPE concentration, took two days. Chemical analyses were conducted over several weeks.

The residues of energetic compounds consisted of RDX, HMX (a manufacturing byproduct of RDX), and TNT (Table 8-2). For the seven tests, 18 large-increment (50–100+) samples (LIS) and four multi-increment (approximately 40) samples (MIS) were taken within the plumes collectively. A minimum of two LISs were taken in each plume, and two MIS samples were taken in two plumes. For the LIS, sample repeatability varied from a factor of 1.1 to a factor of 8.1. The adjacent MIS samples were closer, within 17 percent of each other (Table 8-3). Except for within the craters, detection of HMX was sporadic, reflecting the small fraction of this explosive within the matrix of Composition B. No TNT was detected. All plume HMX quantities were near the detection limits for the instrumentation, making within-plume comparisons of LIS impractical.

	НМХ			RDX			
Sample Type	M _R (µg)	C _s (µg/m²)	M _τ (μg)	M _R (µg)	C _s (µg/m²)	M _T (μg)	
			Plume 1				
LIS	1.3	1.4	1800	7.3	7.7	9800	
LIS	2.6	2.6	3300	17	17	21000	
Mean			2500			15000	
			Plume 2				
LIS		T_	T-	3.1	3.1	5400	
LIS	_	_	_	_	1.2	2100	
LIS	-	_	_	3.3	3.3	5800	
Mean			_			4400	
			Plume 3				
MIS	T-	—	T	1.9	4.8	8800	
MIS		_	_	3.6	4.0	7300	
Mean (MIS)			1_			8000	
LIS	_	1_	_	1.3	1.3	2300	
LIS	2.0	2.0	3700	2.6	2.6	4800	
Mean (LIS)						3600	
			Plume 4				
LIS	3.3	3.1	5200	33	32	53000	
LIS	_	_	_	15	14	23000	
LIS	_	_	_	4.3	4.1	6700	
Mean						27000	
			Plume 5				
MIS	<u> </u>	_		5.4	6.0	9900	
MIS	T	Ī-	_	5.5	6.1	10000	
Mean (MIS)			_			10000	
_IS	_	_	_	21	21	34000	
LIS	0.48	0.44	710	22	20	32000	
Mean (LIS)						33000	
			Plume 6				
LIS	-	1-	T-	0.39	0.35	590	
_IS	_	-	-	2.9	2.8	4600	
JIS	-	-	_	0.44	0.34	570	
Mean			_			1900	
		, <u> </u>	Plume 7	-			
_IS	_	T-	_	3.5	3.2	5000	
_IS	1.5	1.2	1800	31	24	37000	
_IS	_		_	19	19	29000	
Vlean			1			24000	

Notes: M_R – Mass recovered from sample, C_S – Sample concentration, M_T – Total mass estimate for

MIS – 40-increment sample
LIS – ≈100-increment sample
(-) Indicates values below the detection limits of analysis instrumentation.
Detection limits of extract: 30µg/L (all constituents)

Table 8-3 Analysis of Multi-Increment Sample Repeatability for RDX					
Plume	Reps	Average (mg)	Range (mg)	Ratio (High to Low)	
LIS					
1	2	15	11	2.1	
2	3	4.4	3.7	2.8	
3	2	3.6	2.5	2.1	
4	3	27	46	7.9	
5	2	33	2.0	1.1	
6	3	1.9	4.0	8.1	
7	3	24	32	7.4	
Avg.		15	14	4.5	
MIS					
3	2	8.0	1.2	1.2	
5	2	10	0.1	1.0	

Field OA results indicate that the plume definitions were accurate and that residues were not missed outside the visible plume during collection. Plume accuracy was determined by sampling outside the demarcated plume (OTP). This was done using two delineation protocols: Sampling an annulus (0-3 m and 3-6 m wide) outside the plume boundary and sampling outside the plume within 10 m of the detonation point and within 10-20 m of the detonation point. One test indicated residues outside the plume in a small area (57 m²) that had been heavily trafficked during sampling within the plume. Residue concentrations in an adjacent, less trafficked zone were an order of magnitude lower, indicating that this OTP sample was likely contaminated by personnel walking through the area. Both subsurface samples taken beneath previously sampled points were blank (Table 8-4).

Table 8-4 Field QA R	esults	A.A.							
	***	НМХ			RDX			TNT	
Sample Type	M _R (μg)	C _s (µg/m²)	M _τ (μg)	M _R (µg)	C _s (µg/m²)	M _τ (μg)	M _R (µg)	C _s (µg/m²)	M _τ (μg)
				Plum	e 1				
OTP-10R	0.67	1.9	2400	23	66	3700	1-	 	-
OTP-20R	_	_	_	0.71	0.97	374	-	_	_
Notes: See Tabl	e 8-2 for hea	adings	Control Control			Maurice -			

OTP - Outside The Plume

R=Radius (m) from detonation point

OTP results for plumes 2-7 were below detection limits (30µg/L).

Crater samples were only briefly examined and are not included in this report. The higher concentration of explosives residues generally found in the craters represents only a very small portion of the area of the plumes (approximately 1 percent) and thus has a smaller than apparent impact on the overall mass of residues from the detonations (Table 8-5). All craters contained residues of HMX and RDX, and one crater contained a detectable trace of TNT.

Table 8-5 Plume Component Dimensions						
	Plume (m²)	Crater (m²)	OTP (m ²)	Crater/Plume (%)	Plume+OTP Plume	
Plume 1	1200	15	440	1.2	1.4	
Plume 2	1600	12	560	0.7	1.3	
Plume 3	1300	11	1200	0.8	1.9	
Plume 4	1200	12	540	1.0	1.5	
Plume 5	1100	11	1200	0.9	2.1	
Plume 6	1400	15	530	1.1	1.4	
Plume 7	1200	13	500	1.1	1.4	
All Tests	1300	13	710	1.0	1.6	

Detonation efficiency was also examined. This was determined by dividing the total estimated mass of residues by the pre-detonation explosives mass. For all tests, the total explosives load was 2724 g TNT, 5388 g RDX, and <1 g HMX. Although HMX is not a constituent of Composition B, up to 485 g (9 percent of the RDX) may be present in the explosives load. The total explosives mass included loads from the projectile, fuze, blasting cap, and C4 donator charge. Consumption efficiencies for load and donor charge for all the rounds were in excess of 99.999 percent, indicating that all the detonations were high order (Table 8-6).

Table 8-6 Detonation Efficiencies of 155-mm BIPs						
Mass recovered (mg) Mass consumed (efficiency)						
НМХ	RDX	Plume Only	Plume + OTP ²			
2.5	15	99.99977%	99.99971%			
-	3.7	99.99995%				
0.92	4.6	99.99993%	_			
1.7	27	99.99962%	_			
0.20	21	99.99972%	_			
-	1.9	99.99997%	-			
0.61	24	99.99967%	_			
5.9	· 97	99.99980%	_			
	Mass HMX 2.5 - 0.92 1.7 0.20 - 0.61	Mass recovered¹ (mg) HMX RDX 2.5 15 - 3.7 0.92 4.6 1.7 27 0.20 21 - 1.9 0.61 24	Mass recovered¹ (mg) Mass co HMX RDX Plume Only 2.5 15 99.99977% - 3.7 99.99995% 0.92 4.6 99.99993% 1.7 27 99.99962% 0.20 21 99.99972% - 1.9 99.99997% 0.61 24 99.99967%			

¹Mass recovered is based on residues concentrations and sampled plume area.

The analysis was repeated (Table 8-2) whenever a concentration seemed out of range. All blanks, duplicates, and spikes were within acceptable analysis limits.

² Includes both area and residues from sampling outside the plume.

[&]quot;-" indicates that no detectable residues were recovered.

Summary and Conclusions

We sampled residue from seven Composition B-filled, fuzed 155-mm howitzer rounds, detonated using a C4 donor charge and the standard blow-in-place method employed by military explosive ordnance disposal personnel. All rounds were detonated within seconds of one another and went high order by both definitions (>50 percent or >99.99 percent of filler consumed). The average mass of unreacted residues ranged between 0.0 and 1.7 mg for HMX (0.84 mg overall average), between 1.9 and 27 mg for RDX (14 mg average), and 0 mg for TNT. Subsurface samples and samples collected outside the demarcated plume indicate that the sampling methods employed captured virtually all of the residues deposited after detonation. Within-plume repeatability of samples was adequate, and estimates of residue deposition among the detonations were within an order of magnitude.

The results from this test indicate that residues resulting from the blowing-in-place of dud 155-mm HE rounds in impact ranges are small on a per-round basis, resulting in deposition rates in the milligram per kilogram range. One breached, undetonated 155-mm HE round will contribute as much residue to the range environment as almost 450,000 properly detonated BIP dud rounds. These rounds, properly blown in place, do not constitute a significant explosive residue load to ranges. Work with smaller-caliber HE rounds, 105-mm howitzer and 81-mm mortar rounds, indicates that properly detonated live-fired rounds have a deposition rate an order of magnitude below that of BIP rounds. Live-fire testing of 155-mm HE rounds will be necessary before this correlation can be tested for the larger rounds.

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9 Summary and Conclusions

Introduction

During FY2004 various approaches to the improvement of surface soil sampling strategies were investigated by sampling on various types of ranges at several locations and by conducting detonation experiment for generation of residues. Characterization of specific types of training ranges continued with sampling at new sites and with revisitation of certain sites that have been sampled previously. Additional tests were initiated to investigate the long-term transport properties of broken rounds generated when UXOs were struck by shrapnel from detonation of a second round. A general picture of the nature and distribution of explosive residues resulting from live-fire training exercises is emerging. Below is (1) a summary of specific finding this year followed by (2) a summary of data gaps filled and remaining in the project to date.

Summary of Specific Findings in 2004

Sampling strategies

The results of an intensive sampling exercise at Ft. Polk, LA, around a low-order detonation reaffirmed that a single surface soil sample cannot represent an area even as small as one square meter when the constituent is in crystalline form. Collection of 25 randomly collected increments was a marked improvement over collection of discrete samples; however, uncertainty remains relatively high. Using a systematic approach to generating composite samples proved more likely to consistently encompass "hot spots" of the size encountered around the low-order detonation. RDX concentrations decreased with distance along a transect from the sampling grid placed over the low-order detonation. This result was in contrast to results at the tank target, where no concentration gradient with distance from the target was observed. The inconsistency is very likely a function of how the munitions impinge on the respective sites. Results of these two studies demonstrate that systematic compositing is a more reproducible approach to sampling than random compositing or discrete sampling.

Low-order detonations

Results of studies in which low-order detonations were generated for the artillery projectiles, 60-mm mortars, and 105- and 155-mm artillery projectiles demonstrate the challenge in designing specific energy yields. Munitions had a tendency to detonate with very low or very high energy yields. Nevertheless, the mass of explosive residue recovered was inversely related to the energy yield based on overpressure measurements. Although the initiating tool was consistently pointed in the same direction, the distribution of the residue was directionally inconsistent. The mass of residue from the 105-mm projectiles tended to increase with distance; however, variability was so high that differences were not significant. No significant difference in residue mass with distance for 155-mm projectiles was observed. The largest particle size fraction, >12.5 mm, tended to predominate, especially with the 60-mm mortars and the 105-mm projectiles. Large chunks predominated over fines (<0.25 mm) in the residues. The ratio of TNT to RDX in pre-detonation Composition B was generally reflected in the post-detonation composition. The results suggest that low-order detonations will contribute to the source term for range residues that are predominantly large particles to chunks of solid Composition B. Therefore, the ratio of TNT to RDX in these chunks is conserved. Transport will depend heavily on dissolution rates of TNT and RDX from the solid composition and subsequent interactions between dissolved constituents and the soil.

Site characterization

Gagetown. Results of the third and final phase of sampling at CFB Gagetown encompassed a propellant burning pad and the following four specific types of ranges: antitank, hand grenade, rifle grenade, small arms. Surface soil samples were analyzed for heavy metals and explosives. Leaching tests (TCLP) were also performed to determine concentrations and bioavailability of metals. Over the course of the three phases of the study, heavy metal concentrations increased. The following metals of concern were identified at the target area of the antitank range: Cu, Ni, and Zn. Ponds in the target area contained Cu, As, Cr, Ni, Pb, and Zn concentrations that exceeded industrial threshold values. Although increasing over time, Cu, Ni, and Zn found in both grenade ranges failed to reach industrial threshold values. High levels of Pb and Sr were detected at the burn pads and at the small arms range. Values for Cu, Zn, and Sb exceeded the industrial threshold at the small arms range. Metal concentrations tended to decrease with soil depth. Almost no energetic residues were detected at either the hand grenade or rifle grenade ranges. At the antitank range, HMX predominated at the target, while NG was detected at high levels at the firing line. The NG was detected to a depth of 60 cm. HMX, TNT, and NG were detected in high concentrations in the ponds located in the target area of the antitank range. The results of a sampling exercise using multiple increments of more than 50 in a large sampling area successfully improved the delineation of energetic residues over smaller increment sampling.

Cold Lake. The results of extensive sampling of soils, surface water, and vegetation at the Cold Lake Air Weapons Range in Alberta indicate minimal contamination. Alpha and Bravo ranges are used primarily for bombs and rockets, and Shaver River and Jimmy Lake ranges for 250-, 500-, 1,000-, and

2,000-pound bombs. The very low concentrations of metals observed in the soils of these ranges are attributable to the very effective practice of frequent debris removal and tilling of the soil. Metal concentrations in surface water of Primrose and Jimmy Lakes were also low, except for elevations in cadmium and copper concentrations in Jimmy Lake. No explosives were found in surface water. However, in the soils of Jimmy Lake range, propellants such as nitroglycerine were found in all samples. This finding suggests the heavy use of rockets. In contrast, on the Shaver River range very little propellant was found, but TNT was found in almost all samples, which suggests heavy use of bombs. With the exception of the high TNT concentrations on the Shaver River range and limited accumulation of metals at the Jimmy Lake range, the Cold Lake ranges exhibited little contamination by metals or explosives.

MMR. During the period of 1 October 2003 through 30 September 2004, environmental investigations continued at Camp Edward on the MMR, where site assessment was initiated in 1997. No new explosives were detected since last year's update presented in CP1155 interim report 4. The most frequently detected explosives (in order of decreasing frequency) are TNT and the amino transformation products of TNT, compounds categorized as "other," perchlorate, dinitrotoluenes, and RDX. Compounds in the "other" category include derivatives and/or components of propellants and of waxes used in inert rounds. Significant decreases in concentrations of the propellant nitroglycerine and compounds listed as "other" were observed this year. Unlike last year, no white phosphorus was detected in any soil sample. Groundwater quality exhibited no change from last year. Predominant contaminants include (in order of decreasing frequency) perchlorate, RDX, HMX, and the amino transformation products of TNT. A shift in focus from characterization/monitoring to remediation was developed this year to lay the foundation for expediting the achievement of remediation goals and to reduce long-term monitoring costs.

Cracked shells as a source term for leaching

Two approaches were developed for generating cracked 81-mm mortars for use in long-term transport studies. In the first, C4 in various amounts and configurations and shaped charges containing C4 in various standoff distances were used. In the second approach a mortar was detonated in proximity to a second mortar to achieve cracking of the second mortar by fragments of the first (sympathetic detonations). Cracking was achieved by placing C4 on the first mortar; however, the shaped charges failed to pierce the shell casing. Detonations with C4 produced cracked shells even when the two mortars were separated by a distance of 157 cm. The shells were cracked not by sympathetic detonation as originally postulated, but by flying shrapnel from the primary detonation. The cracked shells are ready for use in leaching experiments (start date: September 17, 2004). These studies will be conducted under unsaturated conditions in Teflon-lined stainless steel soil columns (60 cm diameter and 75 cm deep).

Blow-in-place detonations of 155-mm projectiles

Seven 155-mm projectiles were detonated on snow-covered ice at Fort Richardson, AK. Detonations were achieved almost simultaneously using standard blow-in-place techniques employed by military explosives ordnance disposal personnel using a block of C4 initiated with a blasting cap. Residues were collected over the visible plume to a depth of 2 cm. Two composite sampling approaches were used, one using 100 increments and one using 40 increments. Melted snow samples were analyzed by HPLC and/or GC methods. All detonations were high-order. The average recovered residual mass was 14 mg for RDX and 0.84 mg for HMX; no TNT was detected. The results for subsurface samples and samples collected beyond the plume suggested that the sampling methods captured most of the residue.

Conclusions

Significant conclusions of the various investigations conducted in 2004 include the following:

- Adequately characterizing the distribution and quantity of the highly distributed scattering of solid residues that are extreme in the range of particle sizes has been a prominent objective of this project. The systematic composite sampling protocol developed for artillery ranges yielded more reproducible results than random composite or discrete sampling protocols.
- Although controlling the energy yield of low-order detonations was challenging, residues were inversely related to energy yields. Directionality was unpredictable and variability was too high to identify statistically significant trends in the distribution of residue mass by distance from the point of detonation. Although large particles (>12.5 mm) predominated, few differences in particle size distribution of residues were significant. The pre-detonation ratio of TNT to RDX was conserved.
- Heavy metal concentrations in surface soils have increased over the course of the three phases of this study at CFB Gagetown. Metals in concentrations of concern in surface soils and in surface water of ponds at the antitank target areas, at hand- and rifle-grenade ranges, or on small arms ranges were primarily Cu, Ni, Zn, As, Cr, Pb, and Sb. Pb and Sr were detected at the burn pads and on the small arms ranges. Metals concentrations tended to decrease with soil depth. Explosives residues varied within the antitank range: HMX predominated at targets, NG at the firing line, and HMX, TNT, and NG in ponds in the target area. Almost no energetic residues were detected at the hand- or rifle-grenade ranges. These data illustrate the potentially dynamic character of residue constituents over time.
- Low concentrations of metals on the ranges at Cold Lake Air Weapons Range are probably attributable to frequent debris removal and tilling of the soil. Metals were found in low concentrations in the surface water of lakes on the ranges, except for one lake where Cd and Cu were elevated. The nature of explosive residues in surface soils was consistent with range use, e.g., propellants

were detected where rockets were used and TNT was found where bombs were used. In general, contamination by metals or explosives was limited on the ranges of this installation.

- A significant decrease in concentrations of nitroglycerin and organic compounds associated with inert rounds was observed at MMR. Groundwater quality exhibited no change since last year. No white phosphorus was detected in soils this year. Future assessments at MMR will shift significantly toward remediation rather than characterization and monitoring.
- Sympathetic detonations effectively generated cracked and broken 81-mm mortars, even when mortars were 157 cm apart. Block C4 was also effective. Cracking was initiated by flying shrapnel rather than by sympathetic detonation. Residues from detonations will be used in column leaching experiments.
- The nearly simultaneous detonation of seven 155-mm projectiles using block TNT, as is common practice for demolition of UXO by military explosive ordnance personnel, resulted in high-order detonations and very little explosive residue. Tests were conducted on snow-covered ice, making the deposition plume visible for sampling. Average mass recovered was as follows: RDX, 14 mg; HMX, 0.84 mg; and TNT, none.

Summary of Data Gaps Filled and Remaining to Date

A summary of data gaps filled and remaining reveals that much has been accomplished in CP1155 (Table 9-1). This study has developed technical protocols for characterizing the explosives residues on various types of training ranges, specifically artillery and grenade ranges and air-to-ground bomb and rocket ranges. The significant database developed in this study provides a realistic reference for estimating the source term of explosives residues for specific types of training. An understanding of the significant contribution of residues associated with low-order detonations and with residues resulting from blow-in-place is under development. The relationships emerging between various training activities and residues of energetic materials provide a basis for sound management strategies that will prevent the training mission from conflicting with environmental stewardship.

The results of the project have also focused attention on the kinds of information yet needed but not yet acquired (Table 9-1). Some of the data gaps are beyond the scope of CP1155 (Table 9-2) but are identified for consideration by others.

Table 9-1					
Summary of Data Gaps Filled and Remaining to Date in CP1155					
Data GAP	Filled	Unfilled	Reference		
I. Distribution of Energetic Residues on the Surface Soil of Various Types of Ranges					
I A. Impact Areas					
Distribution and concentrations of HMX and TNT at antitank rocket range impact areas.	Four antitank range impact areas were studied. Residues are mainly from ruptured LAW rockets. HMX is often present at >1000 mg/kg and is 100 times the concentration of TNT. The distribution of residues is spatially heterogeneous; however, a declining concentration gradient extends from targets.	Residue particle size distribution.	ERDC TR-02-8 ERDC TR-03-2 ERDC/CRREL TR-04-7 ERDC TR-04-4 DRDC TR 2003-152 DRDC TR 2003-208 MMR-1903		
Distribution and concentrations of RDX and TNT at hand grenade ranges.	Ten hand grenade ranges were studied. The major sources of energetic residues are from low-order detonations or duds that are blown in place with C4. RDX and TNT concentrations are often in the low mg/kg range.	Residue particle size distribution.	ERDC/CRREL TR-01-5 ERDC TR-01-13 ERDC TR-03-2 ERDC TR-04-4 DRDC TR 2003-152		
3. Distribution and con- centrations of residues of energetic compounds at artillery range impact areas.	The residues of energetic compounds within artillery impact ranges are largely present as small distributed point sources from low-order detonations and breached casings of artillery and mortar rounds. Most of the impact range is uncontaminated, but chunks of pure explosive (TNT, Composition B) and soil concentrations in the percent level are present.	Distance and concentration gradient of residues from targets and/or craters.	ERDC/CRREL TR-01-5 ERDC TR-01-13 ERDC TR-02-8 ERDC TR-04-4 DRDC TR 2003-152 MMR-4217 MMR-3915 MMR-3439		
4. Distribution and con- centrations of residues of energetic compounds at Air Force bombing ranges, missile ranges, and rocket ranges.	Only one Canadian Air Force HE bombing range has been sampled. TNT from tritonal was found to be widespread in the tens of mg/kg.	Additional sampling at U.S. Air Force ranges is needed to determine if the results obtained at the Canadian range are typical of U.S. ranges.	DRDC TR-2003-208 DRDC TR-2004-204 ERDC TR-04-4		
5. Distribution and con- centrations of residues of energetic compounds at naval air ground ranges.	Cold Lake Air Weapon ranges in Canada have been fully characterized.	No sampling of Navy impact ranges has been conducted on U.S. ranges. Sampling at naval ranges is necessary to understand whether there is substantial accumulation of energetic residues.	DRDC-TR-2004-204 DRDC-TR-2003-208		
			(Continued)		

Table 9-1 (Contin	Table 9-1 (Continued)					
Data GAP	Filled	Unfilled	Reference			
IB. Firing Points						
Distribution and concentrations of propellants at antitank rocket range firing points.	Six antitank range firing points were studied. Residues occur as slivers of unconsumed propellant ejected from the rocket motor. NG is present in surface soils in front of and behind the firing line. The highest concentrations of NG (up to 0.2 percent) have been found behind the firing line.	The quantity and distribution of nitrocellulose and perchlorate. Results suggest a high level of contamination resulting from firing. This should be examined in more detail, with witness plates associated with firing. Environmental load per firing per type of munition should be measured. Also, the health impacts on soldiers should be examined, since they might be exposed to contaminated dust upon firing.	ERDC TR-02-8 ERDC/CRREL TR-04-7 ERDC TR-03-2 ERDC TR-04-4 DRDC TR 2003-152 DRDC TR 2003-208 MMR-1903			
Distribution and concentrations of propellant residues at artillery and mortar range firing points.	NG and 2,4-DNT have been frequently detected at artillery and mortar firing points. These energetic compounds are retained (long half-lives), within unconsumed fibers and slivers of nitrocellulose. Detectable concentrations of these residues can be found up to 100 m from the firing point. Concentrations of NG and 2,4-DNT can be as high as the tens of mg/kg.	Quantity and distribution of residues of nitroguanidine, nitrocellulose, and perchlorate at firing points of mortars and various artillery calibers (e.g., 2.75-inch rockets and 155-mm) of howitzer by sampling immediately after firing. Witness plates trials should be conducted for many types and calibers of weapons to learn more about their respective environmental impacts.	ERDC/CRREL TR-01-5 ERDC TR-01-13 ERDC TR-02-8 ERDC/CRREL TR-04-3 ERDC TR-04-4 DRDC TR 2003-152 DRDC TR-2004-205 MMR-4342			
IC. Demolition Ranges	100000000000000000000000000000000000000					
Distribution and concentrations of residues of energetic compounds at demolition ranges.	Only a few demolition ranges have been evaluated, but the demolition range at MMR is a major source zone for groundwater contamination with RDX, HMX, ADNTs, and perchlorate. Studies at two other demo ranges have confirmed the presence of RDX in surface soils, likely from use of C4.	Sampling at additional demolition ranges is needed to better understand the potential for off-site migration of residues from these types of ranges. Energetic compounds were identified in runoff at one demolition range.	ERDC TR-04-4 Draft MMR Link report, MMR- 8830 ERDC TR-03-2 MMR-4158			
II. Sampl	ing Considerations when Character	rizing Distribution of Residues	on Firing Ranges			
II A. Sampling Approach	es and Protocols					
Sampling strategies to obtain representative surface soil samples at antitank rocket ranges.	At antitank rocket ranges the impact areas and firing points should be characterized using a multi-increment sampling strategy. Different sampling designs should be used in these two areas since concentration gradients are anticipated around the target and either side of the firing line. Around the target the area should be divided into concentric circles or segmented halos. Sampling should be performed directly in front of and behind the firing line using a segmented area design.	USACE protocol or guideline for representative sampling at antitank rocket ranges.	CRREL Special Report 98-9 ERDC TR-02-8 ERDC/CRREL TR-04-7 Jenkins et al. (in press) Ramsey and Hewitt (in press)			
			(Continued)			

Table 9-1 (Contin	Table 9-1 (Continued)				
Data GAP	Filled	Unfilled	Reference		
2. Sampling strategy to obtain representative surface soil samples at hand grenade ranges.	Multi-increment samples should be collected to estimate the average concentration of energetic residues in impact areas. The entire impact area can be treated as a single decision unit or a segmented area sampling design can be used to determine if there are concentration gradients.	USACE protocol or guideline for representative sampling at hand grenade ranges.	ERDC/CRREL TR-01-5 ERDC TR-01-13 ERDC TR-03-2 ERDC/CRREL TR-03-16 ERDC TR-04-4		
3. Sampling strategy to characterize the firing points at artillery/mortar ranges.	Multi-increment samples should be collected to estimate the average concentration of energetic residues at firing points. The entire impact area can be treated as a single decision unit or a segmented area sampling design can be used to determine if there are concentration gradients.	USACE protocol or guideline for representative sampling at artillery/mortar ranges. More depth sampling should be conducted to better assess the vertical profiling concentrations of contaminants.	ERDC/CRREL TR-01-15 DRDC TR 2003-152 ERDC/CRREL TR-05-XX Hewitt et al. (in press) Jenkins et al. (in press) Ramsey and Hewitt (in press)		
4. Sampling strategies to characterize the impact areas at artillery/mortar ranges and Air Force bombing ranges.	At artillery and Air Force impact ranges, partial detonations can in some cases be visually located. Chunks of energetic residues should be weighed. A multi-increment sampling strategy should be used to establish energetic residue soil concentration to estimate the mass loading. A segmented halo sampling design should be used to establish the area affected by energetic residues.		ERDC/CRREL TR-04-14 ERDC/CRREL TR-05-XX Hewitt et al. (in press) Jenkins et al. (in press) Ramsey and Hewitt (in press) DRDC TR-2004-205 DRDC TR-2003-152 DRDC TR-2004-204 DRDC TR-2003-208		
II B. Sample Processing					
Particle size distribution of energetic residues present in surface soil samples from training ranges.	Surface soil samples from firing points and impact areas often contain particles of energetic residues larger than 0.6 mm. Samples should be sieved to 2.0 mm to capture the energetic residues in this soils.	An increase in sample size from 2 to 10 g should be made for Method 8330 and 8095 for characterizing military training ranges.	FATE Encyclopedia www.ttclients.com/encyclopedia ERDC TR-04-4		
2. Strategies to maintain representativeness of energetic residues in multi-increment samples.	Large multi-increment samples must be thoroughly mixed (homogenized) prior to subsampling. This can be achieved by grinding the entire sample to a fine powder. Samples containing propellant residues require a longer grinding period than samples containing high explosives. Another large sample homogenization technique, whereby the sample is mixed with acetone to make a slurry, relies on dissolving the energetic residues and deposits them onto the soil grains. Replicate subsamples must be taken to demonstrate that sample mixing has been achieved.	A modification to the sample processing should be addressed in Method 8330 and 8095 for characterizing military training ranges. Moreover, alternative sample processing methods should be evaluated. The effects of removing vegetation from samples should be evaluated.	Walsh et al. (2003) ERDC/CRREL TR-01-15 FATE Encyclopedia www.ttclients.com/encyclopedia ERDC CRREL TR-05-XX (Bjella, Lambert and Perron, in press)		
			(Continued)		

Data GAP	Filled	Unfilled	Reference
I C. Analytical			
Analytes not included the standard EPA Method 8330		Modifications to Method 8330 are necessary to add to the standard analyte list, i.e. NG, PA, DANT, MNX, DNX, TNX	
2. Method confirmation	Method 8330 should be modified to recommend the use of a photo diode array (PDA) to confirm uncertain analytical results from the primary/secondary columns		
	III. Residues Associated	with Specific Firing Events	
II A. Residues from Hig	h-Order Detonation of Fired Round	3	
Mass of unconsumed RDX and TNT from the ive-fire detonation of Composition B high explosive (HE) 40-mm ifle grenades.	RDX and TNT were detected in the detonation residues. The average mass of RDX for three replicates was 1.6 mg, or 8×10^3 percent of the original mass. The average mass of TNT was 0.0052 mg, or 4×10^{-5} percent of the original mass.		ERDC/CRREL TR-03-16 ERDC TR-04-4
2. Mass of unconsumed RDX and TNT from the ive-fire detonation of Composition B HE M67 nand grenades.	RDX was detected in the detonation residues. The average mass of RDX for seven replicates was 0.025 mg, or 2 × 10 ⁻⁵ percent of the original mass.		ERDC/CRREL TR-03-16 ERDC TR-04-4
3. Mass of unconsumed RDX and TNT from the ive-fire detonation of Composition B HE 60- mm mortar.	Only RDX was consistently detected in the detonation residues. The average mass of RDX for seven replicates was 0.10 mg, or 5 × 10 ⁻⁵ percent of the original mass.		Jenkins et al. (2002) ERDC/CRREL TR-03-16 ERDC TR-04-4
Mass of unconsumed RDX and TNT from the ive-fire detonation of Composition B HE 81-mm mortar.	RDX and TNT were detected in the detonation residues. The average mass of RDX for fourteen replicates was 8.5 mg, or 2×10^{-3} percent of the original mass. The average mass of TNT was 1.1 mg, or 3×10^{-4} percent of the original mass.		ERDC/CRREL TR-03-16 ERDC TR-04-4
5. Mass of unconsumed RDX and TNT from the ive-fire detonation of Composition B HE 120-mm mortar.	RDX and TNT were detected in the detonation residues. The average mass of RDX for seven replicates was 4.2 mg, or 2×10^{-4} percent of the original mass. The average mass of TNT was 0.32 mg, or 2×10^{-5} percent of the original mass.		ERDC/CRREL TR-03-16 ERDC TR-04-4
5. Mass of unconsumed RDX and TNT from the ive-fire detonation of Composition B HE 105- mm howitzer round.	RDX and TNT were detected in the detonation residues. The average mass of RDX for seven replicates was 0.095 mg, or 7×10^{-6} percent of the original mass. The average mass of TNT was 0.17 mg, or 2×10^{-6} percent of the original mass.		ERDC/CRREL TR-03-16 ERDC TR-04-4
			(C

Table 9-1 (Continued)				
Data GAP	Filled	Unfilled	Reference	
7. Mass of unconsumed RDX and TNT from the live-fire detonation of Composition B HE 155- mm howitzer round.			Live-fire trials scheduled for win ter of 2004-05.	
Mass of unconsumed TNT from the live-fire detonation of TNT HE 155-mm howitzer round.			Live-fire trials scheduled for win ter of 2004-05.	
II B. Residues from Blo	ow-in-Place Demolition of Specific M	lunitions		
Mass of unconsumed RDX from the EOD detonation of a 1.25-lb block of C4.	RDX was detected in the detonation residues. The average mass of RDX for eight replicates was 15 mg, or 3×10^{-3} percent of the original mass.		ERDC/CRREL TR-03-16 ERDC TR-04-4	
2. Mass of unconsumed RDX and TNT from the EOD detonation of 81-mm Composition B filled mortar with a 1.25-lb block of C4.	RDX was detected in the detonation residues. The average mass of RDX for seven replicates was 130 mg, or 1 × 10 ⁻² percent of the original mass.		et al., in press)	
3. Mass of unconsumed RDX and TNT from the EOD detonation of Comp B HE 105-mm howitzer round with a 1.25-lb block of C4.	RDX was detected in the detonation residues. The average mass of RDX for seven replicates was 41 mg, or 2 × 10 ⁻³ percent of the original mass.		ERDC/CRREL TR-05-XX (Walsh et al., in press)	
4. Mass of unconsumed RDX and TNT from the EOD detonation of Comp B HE 155-mm nowitzer round with a 1.25- Ib block of C4.	RDX was detected in the detonation residues. The average mass of RDX for seven replicates was 15 mg, or 2×10^4 percent of the original mass.		et al., in press)	
5. Mass of unconsumed RDX and TNT from the EOD detonation of TNT HE 155-mm howitzer round with a 1.25-lb block of C4.	RDX and TNT were detected in the detonation residues. The average mass of RDX for seven replicates was 5.1 mg, or 9×10^{-4} percent of the original mass. The average mass of TNT was 12 mg, or 2×10^{-4} percent of the original mass.		et al., in press)	
3. Residues associated vith blow-in-place lemolition of UXO	Seven replicates of 155-mm artillery projectiles were detonated with C4 on snow cover in Alaska. Seven replicates of two artillery rounds (105- and 155-mm) and two mortars (60- and 81-mm) were detonated with four donor charges (block C4, shaped charges, kinepak binary, and block TNT) at Redstone Arsenal, Huntsville, AL.		Alaska studies are reported in Chapter 8 of this report. Redstone studies are leveraged with Army EQI funds and will be completed in FY2005.	
r. Optimal secondary charge for BIP of heavy artillery rounds and nortars to minimize esidues	Optimization of the secondary charges choice and configuration are planned for FY2006 under EQI funding		Will be reported in FY2006/07 under EQI funds.	
			(Continued	

Table 9-1 (Contin	Filled	Unfilled	Reference
	ed with Low-Order Detonations of S	100 may	
Nestudes Associated Ness and particle size distribution of residues from low-order detonations of heavy artillery munitions.	Testing of four rounds (60- and 81-mm mortars, 105 and 155-mm artillery projectiles) were conducted at various energy yields. The residues were recovered as a function of distance from the detonation. Particle size distribution was determined by sieving of residues.	pecine municins	ERDC TR-03-2 Chapter 3 (this report) Completion report in FY2005 Testing and reporting will be completed in FY2005. Optimization studies under EQI funding are scheduled for FY2006. Taylor et al. (2004)
III D. Residues Associat	ed with Unconfined Charge		
Residues associated with blow-in-place demolition of unconfined UXO	In a worst-case scenario in which unconfined explosive residues were detonated, minimal residues were produced from high-order detonations.		DRDC TR-2003-370
III E. Residues Generate	ed by Sympathetic Detonations		
The contribution of sympathetic detonation to explosive source term on range	Detonation or rupturing of a round by fragments from the detonation of another round near the first is considered <i>sympathetic</i> detonation or rupture. Many such ruptured and broken rounds were generated by blow-in-place detonation of 81-mm mortars. Various standoff distances and test configurations of both C4 and shaped charges were used to detonate the primary round.	Similar trials should be conducted with other munitions to determine their response to fragments from incoming rounds.	Chapter 7 in this report.
	IV. Fate and Transport Pro	cesses of Energetic Residue	S
IV A. Soil/Water Partitio	ning Process Descriptors		
Adsorption coefficients, i.e., Kds, and transformation rates for primary high explosives	Literature review revealed adequate data for TNT and RDX but insufficient data for TNT transformation products and several other explosives and explosives-related compounds		ERDC TR-01-13 ERDC TR-02-10 Pennington and Brannon (2002) ERDC TR-03-02
2. Adsorption coefficients and transformation rate coefficients for 2,4DNT and 2,6DNT, 1,35TNB, and 1,3DNB	Determined by laboratory batch studies in one surface and two aquifer soils		ERDC TR-02-10
3. Process descriptors for transformation products of RDX (MNX, DNX, TNX) and nitroglycerin (NG)	Adsorption kinetics, desorption kinetics, and partition coefficients were determined on these compounds in two surface and one aquifer soil		ERDC TR-02-8 Brannon et al. (2002)
Process descriptors for tetryl and PETN	Adsorption /transformation rate coefficients and adsorption coefficients, i.e., Kds, were determined for these compounds in two surface and one aquifer soil		ERDC TR-03-02
			(Continued

partition coefficients, and transformation rate coefficients were determined for these compounds in diphenylamine, N-nitrosodiphenylamine, and ethyl centralite of E. Effects of E. band p.H. on degradation of perchlorate of the second of t	Data GAP	Filled	Unfilled	Reference
surface soils at 3 pH (5.5, 7.0, 10.0) and two Eh values (+500 and -150 mV). 7. Effects of Eh and pH on degradation of nitroglycerin in high-and low-carbon groundwater slurines was monitored for 14 days under oxidized and reduced conditions at pH 6, 7, and 8. Nitroglycerin remained in solution only at pH 6 under aerobic conditions. Concentrations in this environment exceeded the EPA's established drinking water standard of 0.005 ppm (0.091 ppm in low-carbon soil). Degradation rates were higher under anaerobic conditions, with concentrations reaching zero within 24 hours. IN B. Dissolution Kinetics I. Rates for TNT, RDX, and HMX IV B. Dissolution Kinetics Compounds tested at three temperatures (10, 20, and 30°C) and three pH values (4.2, 5.7, and 6.2) with constant surface area and stirring rate Dissolution kinetics for perchlorate, NG, DNT, and NQ. If the properties of NG at depth on finitized to understand the presence of NG at depth on finitized to understand the presence of NG at depth on finitized to understand the presence of NG at depth on finitized to understand the presence of NG at depth on finitized to understand the presence of NG at depth on finitized to understand the presence of NG at depth on finitized to understand the presence of NG at depth on finitized to understand the presence of NG at depth on finitized to understand the presence of NG at depth on finitized to understand the presence of NG at depth on finitized to understand the presence of NG at depth on finitized to understand the presence of NG at depth on finitized to understand the presence of NG at depth on finitized to understand the presence of NG at depth on finitized to understand the presence of NG at depth on finitized to understand the presence of NG at depth on finitized to understand the presence of NG at depth on finitized	5. Process descriptors for nitrobenzene, perchlorate, nitroguanidine, diphenylamine, N- nitrosodiphenylamine, and ethyl centralite	partition coefficients, and transfor- mation rate coefficients were determined for these compounds in		ERDC TR-04-4
and low-carbon groundwater slurries was monitored for 14 days under oxidized and reduced conditions at pH 6, 7, and 8. Nitroglycerin remained in solution only at pH 6 under aerobic conditions. Concentrations in this environment exceeded the EPA's established drinking water standard of 0.005 ppm (0.091 ppm in low-carbon soil). Degradation rates were higher under anaerobic conditions, with concentrations reaching zero within 24 hours. IN B. Dissolution Kinetics I. Rates for TNT, RDX, and HMX IV B. Dissolution Kinetics I. Rates for TNT, RDX, and HMX IV B. Dissolution Kinetics I. Rates for TNT, RDX, and HMX IV B. Dissolution Kinetics I. Rates for TNT, RDX, and HMX IV B. Dissolution Kinetics I. Rates for TNT, RDX, and G.2) with constant surface area and stirring rate II Rates for explosives compositions In three compositions were tested (Octol, Composition B, and LX14) at various temperatures (10, 20, 30°C) and at constant surface area and stirring rate In three compositions were tested (Octol, Composition B, and LX14) at various temperatures (10, 20, 30°C) and at constant surface area and stirring rate I. Relationships between laborate various and field-derived rates are unknown. In the composition B, and LX14) at various temperatures (10, 20, 30°C) and at constant surface area and stirring rate I. Relationships between laborate various degree of weathering that control rates are unknown. In the composition B, and LX14) at various temperatures (10, 20, 30°C) and at constant surface area and stirring rate I. Relationships between laborate various degree of weathering that control rates are unknown. In the composition B, and LX14, and 30°C) over a period of 14 days. II three temperatures (10, 24, and 30°C) over a period of 14 days.	on degradation of	surface soils at 3 pH (5.5, 7.0, 10.0) and two Eh values (+500 and -150		ERDC TR-04-4
peratures (10, 20, and 30°C) and three pH values (4.2, 5.7, and 6.2) with constant surface area and stirring rate Chlorate, NG, DNT, and NQ. ERDC TR-02-8 Lynch et al. (2001, 2003) Lynch, Brannon and Delfino (2002a, b) Relationships between laboratory and field-derived rates are unknown. Meteorological impacts as well as degree of weathering that control rates are unknown. Solubility of diphenylamine, N- nitrosodiphenylamine, Solubilities were determined at three temperatures (10, 24, and 30°C) over a period of 14 days.	on degradation of	and low-carbon groundwater slur- ries was monitored for 14 days under oxidized and reduced condi- tions at pH 6, 7, and 8. Nitroglycerin remained in solution only at pH 6 under aerobic condi- tions. Concentrations in this envi- ronment exceeded the EPA's established drinking water standard of 0.005 ppm (0.091 ppm in high- carbon soil and 0.14 ppm in low- carbon soil). Degradation rates were higher under anaerobic conditions, with concentrations	compositions should be initiated to understand the presence of NG at depth on firing position. Does the NG exude from the NC matrix and move, or does fine propellant powder penetrate	Yost (2004)
peratures (10, 20, and 30°C) and three pH values (4.2, 5.7, and 6.2) with constant surface area and stirring rate Chlorate, NG, DNT, and NQ. Chlorate, NG, DNT, and NQ.	V B. Dissolution Kineti	cs		
(Octol, Composition B, and LX14) at various temperatures (10, 20, 30°C) and at constant surface area and stirring rate (Octol, Composition B, and LX14) at various temperatures (10, 20, 30°C) and at constant surface area and stirring rate (ERDC TR-02-8 Lynch et al. (2002b, 2003) (ERDC TR-04-4 Lynch et al. (2002b, 2004)		peratures (10, 20, and 30°C) and three pH values (4.2, 5.7, and 6.2) with constant surface area and		ERDC TR-02-8 Lynch et al. (2001, 2003) Lynch, Brannon and Delfino
amine, N- three temperatures (10, 24, and nitrosodiphenylamine, 30°C) over a period of 14 days.		(Octol, Composition B, and LX14) at various temperatures (10, 20, 30°C) and at constant surface area	ratory and field-derived rates are unknown. Meteorological impacts as well as degree of weathering that control rates are	ERDC TR-02-8
and ethyl centralite	amine, N-	three temperatures (10, 24, and		ERDC TR-04-4

Table 9-1 (Contin	ued)		
Data GAP	Filled	Unfilled	Reference
IV C. Photolysis			
Effects of photolysis on explosives residuals on surface soils.	Characterization of extractable photo products of TNT by using negative ion electrospray ionization ion trap mass spectrometry (ESI-MS) in addition to standard HPLC analyses. Characterization of insoluble residue from aqueous TNT photolysates by liquid state nuclear magnetic resonance (NMR) and by infrared, elemental, and molecular weight analyses. Characterization of photo products on weathered chunks of TNT and Composition B by solid state NMR. Characterization of aqueous photolysates of RDX and HMX by NMR, HPLC and/or ESI-MS.	Photolytic properties of DNT, NG, NQ, and perchlorate	Scheduled for FY2005.
IV D. Transport Behavio	r of Energetics and Energetic Form	ulations	
Fate and transport of explosives	Large-scale lysimeter columns studies with broken Composition B containing rounds generated in sympathetic detonations studies are on-going. Transport properties of solution and solid phase explosives and explosive compositions in soil columns under saturated and unsaturated conditions are being studied under EQI funding.	Similar large-scale studies should be conducted with various weapons having various explosive filling (e.g., Composition B, Octol, TNT).	For large-scale study, see Chapter 7 in this report. EQI data will be available in FY2006
IV E. Metals Associated	with Firing Ranges		
Provide an initial assessment of the nature of metal contamination associated with various live-fire range activities	Metal analyses have been system- atically conducted on various Army and Air Force range in Canada	Specific metal species associated with each types of range should be determined. Potential mobility of these species under various envi- ronmental conditions should be reviewed and data gaps filled.	DRDC-TR-2004-205 DRDC-TR-2003-152 DRDC-TR-2004-204 DRDC-TR-2003-208
IV F. Organic Contamina	ants Other than Explosives Associa	ted with Firing Ranges	
Organic contaminants other than explosives associated with firing ranges	Selected composite samples of soils from various ranges investigated in the characterization studies were analyzed for an extensive list of organic contaminants selected on the basis of detections at the MMR.		Report scheduled for FY2005
IV G. Mobilization Asses	ssment Based on Field Observation	s	
An initial assessment of the mobility of energetic and propellant compounds occurring in the field	Lysimeter and monitoring well sam- ples from MMR indicate some ener- getic compounds below surface soils	Define energetic compounds in subsurface soils, ground-water and surface water. Define processes that control mobility based on lysimetry at target locations and firing points	MMR report scheduled for FY2005. Work in progress under Army EQI program
		THE STATE OF THE S	(Continued,

Table 9-1 (Concluded)					
Data GAP	Filled	Unfilled	Reference		
2. The distribution and concentration of energetic compounds in surface and groundwater	Groundwater sampling from a limited number of sites such as MMR and Fort Lewis suggest some energetic compounds are mobile enough to reach the aquifers	Studies should be conducted to assess energetics in surface and groundwater	Various MMR reports ERDC TR-01-13 Surface runoff work is in progress under Army EQI program		
	V. P	rotocols			
Protocol for firing range characterization and management	A site characterization protocol has been developed under The Technical Cooperative Program (TTCP) Key Technical Area (KTA) 28. A website for this KTA will soon be on line. An outline has been completed for range characterization protocol.		KTA website (https://doc-gate.drenet.dnd.ca) USACE protocol/guidance document will be available Jan 2006.		

Table 9-2 Data Gaps bey	ond the Scope of CP1155
1. Health risks to the soldier in the field	Propellant residues/health risks. Based on the residues observed at firing positions, gunners may be regularly exposed to burned propellant dust. The dust can be composed of many things, including PAHs, micron-sized particulates of various compositions, and NC fibers imbibed with NG and 2,4 DNT. Air sampling should be conducted at firing positions to learn more about soldier exposure. Propellant residues in closed firing scenarios. Tank firing potentially allows accumulation of high levels of propellant residues inside the tank, which is a completely closed vessel. Wiping of tank interiors before and after firing and air sampling should be conducted in tanks. Small arms firing lines. Various concentrations of lead and NG have been observed in the surface soils at small arms firing lines. Soldiers often lie on the ground when firing and are, therefore, in close contact with potentially contaminated soil. The potential adverse health impact should be determined.
2. Surface water	Ponds in impact area. Often the highest levels of contaminants are found in the sediment and water of ponds in the impact areas of antitank ranges. Surface water runoff in impact area should be controlled to prevent the migration of contamination from this source.
3. Range design	Grenade ranges. Various contaminants (RDX, TNT, TNT derivatives, Cu, Zn, and Cd) accumulate in grenade ranges. Since grenade ranges are not very large, an underground catchment system for capturing contaminants should be designed and adopted. Such a system would protect surface and groundwater.
4. Remediation	Small arms ranges. Very high levels of lead and other heavy metals are detected in the small arms range firing berms. Results of TCLP tests demonstrate that these metals are leachable. Treatment techniques are needed to immobilize these metals in the berm to prevent migration to ground and surface water and uptake by vegetation. Firing positions. Remediation methods should be studied to decontaminate firing positions. Lime treatment is a promising option. Small-scale studies could be undertaken followed by field trials. Real-time sensors. Because of the large size and possibility of surface vegetation on artillery/mortar ranges and Air Force bombing ranges, a real-time sensor would facilitate the detection of areas with high concentrations of energetic residues. The relationship between residues and crater/UXO density should be assessed to evaluate the utility of airborne sensor technologies (e.g. digital infrared photogrammetry, LiDAR, HIS, SAR) for initial range assessment and for guiding field sampling.
5. TCLP testing	Metals in impact area. Grenade ranges, antitank impact area and artillery range impact areas present concentrations of concern for various heavy metals. No TLCP tests have been conducted to define the potential for migration of these metals. Future sampling should include TCLP testing.
6. Corrosion rate of metal casing material of munitions	A database of all DoD munitions that specifies periods of use, metal casing compositions, wall thickness, etc., should be developed.

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13. SUPPLEMENTARY NOTES

14. ABSTRACT

The potential for generation of environmental contamination in the form of residual munitions constituents during live-fire training activities on military ranges is a significant concern. The objectives of this project were to determine the nature and distribution of the potential contamination and to define transport properties of the constituents. Surface soils associated with impact craters, targets areas, and firing points on U.S. and Canadian ranges were investigated. Residues from high-order, low-order, unconfined charge, and blow-inplace detonations were characterized. Analyses of these residues defined concentrations and spatial distributions of munitions constituents under various firing activities for specific munitions. Special emphasis was placed on developing representative sampling strategies. Residues from low-order detonations were assayed to develop a source term for use in fate and transport models and risk assessment models. Pertinent data from the Massachusetts Military Reservation was reviewed and compared to the database for other ranges. Results demonstrate that a systematic composite sampling protocol developed for artillery ranges improved reproducibility over random composite or discrete sampling protocols. Results of low-order detonation studies confirmed an inverse relationship between energy of detonation and residue generated. While directionality was unpredictable, the residue was dominated by larger particles, which resulted in conservation of the pre-detonation composition of the munition. Several heavy metals were of significant concern at antitank target areas, hand- and rifle-grenade ranges, and small arms ranges. (Continued)

15. SUBJECT TERMS

See reverse.

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14. ABSTRACT (continued)

Explosives detected were specific to range activity. Results of sympathetic detonation tests demonstrated that cracking was initiated by flying shrapnel rather than by the shock wave of the first detonation. High-order detonations generate by blow-in-place detonations resulted in low-milligram quantities of explosives residue. The results of this project define the relationship between various training activities and residues of energetic materials, which provides a basis for sound management strategies supporting training range sustainment without conflicting with objectives of environmental stewardship.

15. SUBJECT TERMS

Blow-in-place
Detonation residues
Dinitrotoluene
Explosives
Fate and transport of explosives
High-order detonations
HMX
Low-order detonations
Propellants
RDX
Sympathetic detonations
Test ranges
TNT
Training ranges